THE INFLUENCE OF LYOPHILE COLLOIDS ON PRECIPITATION FROM SOLUTION

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INTRODUCTION

In the formation of a precipitate by the interaction of substances in aqueous solution, three main processes of localisation of the material composing the solid phase may be recognised. There is first the appearance of "crystallisation" centres or nuclei, around which the rest of the insoluble substance accumulates. The growth of these nuclei by the accretion of atoms, molecules, or ions constitutes a second process. In the third place we may have union of the "primary" particles to form larger masses.

It is well established (1) that the presence of gelatin or other lyophile colloid tends to suppress the second and third of these processes owing to adsorption of the colloid to form a thin film on the surface of the crystals or particles of solid. The influence of gelatin and the like upon the formation of nuclei has, on the other hand, received little attention, but it is reasonable to suppose that an inhibitive action is probable here also. It appears likely that in the presence of, for example, gelatin, only extremely small transitory nuclei would be formed, since, due to the adsorption of "gelatin" upon them, they would fail to grow and in consequence of their high solubility would speedily disintegrate. Under these conditions the solution would become super-

(1) Freundlich "Kapillarchemie" Vol.II(1932)460-462.

saturated with respect to the "insoluble" product of the reaction.

As is well known, Wi.Ostwald[1] suggested that such supersaturation might explain the formation of Liesegang rings of silver chromate by the interaction of silver nitrate and potassium chromate in the presence of gelatin. Ostwald's theory has given rise to much discussion, based mainly, however, on observation on the periodic precipitation itself. Williams and Mackenzie[2] appear to have been the first to attempt to obtain direct evidence of the actual occurrence of supersaturation. These workers found that if equivalent solutions of silver nitrate and potassium chromate were mixed in the presence of gelatin, the resulting mixture remained clear yellow for a time and then became red. At a sufficiently high concentration of gelatin, the change was delayed for 72 hours, though the concentration of the silver chromate was much higher than in a pure saturated aqueous solution at the same temperature. It was observed that the silver chromate in the yellow systems diffused more like a crystalloid than a colloid and hence was believed to be present in true solution, though highly supersaturated. The appearance of a red colour was attributed to the formation

(1) Wi.Ostwald, Z.physikal.Chem., 27 (1897) 265: "Lehrb.d.allgem.Chem.," Leipzig, 2nd Edn. (1899) 2, 778.

(2) Williams and Mackenzie, J.C.S., 117 (1920) 844.

of solid silver chromate by "release" of the supersaturation. Sen and Dhar[1] reported that they were unable to reproduce the diffusion phenomena observed by William and Mackenzie, but the work of the latter was, in the main, confirmed by Bolam and Mackenzie.[2]

Bolam and Mackenzie[3] have obtained even more striking evidence of supersaturation by measuring the potentials developed by a silver electrode immersed in the silver chromate-gelatin mixtures. These measurements showed that prior to the appearance of the red colour, the activity of the silver ion remained constant at a value much higher than in a saturated solution of silver chromate at the same temperature. On the appearance of the red colour there was a corresponding decrease in the activity of the silver ion. In a recent paper Nabar and Desai[4] give an account of similar results in systems containing hydrolysed gelatin. Bolam and Mackenzie (loc.cit.) further determined the conductivities of the yellow systems and found that they also could be explained on the supposition that the yellow mixtures contained silver chromate in supersaturated solution. There

(1) Sen and Dhar, Kolloid Zeitschr., 34 (1924) 270.

(2) Bolam & Mackenzie, Trans.Farad.Soc., 22 (1926)151.

(3) Bolam & Mackenzie, Ibid., 22 (1926) 162.

(4) Nabar and Desai, Ibid., 28 (1932) 449.

are therefore strong grounds for regarding the red colour as due to the actual formation of the solid phase, rather than to the coagulation of pre-existent solid colloidal particles of silver chromate.(1)

The potentiometric data of Bolam and Mackenzie indicate that the activity of the silver ion in a yellow silver chromate-gelatin system may be much less than in a pure aqueous solution of silver nitrate containing the same amount of silver. This result admits of the following possible explanations - (1) combination of part of the silver uon with the gelatin, (2) interionic action between the silver ion and the chromate ion or the ionised gelatin, (3) separation of part of the silver as colloidal silver chromate (2). More than one of these effects may, of course, be present. None of them, however, is inconsistent with the formation of a relatively stable supersaturated solution by part, at least, of the silver chromate. The first object of the present investigation was to ascertain how far these factors are involved. In other words, the attempt has been made to account <u>quantitatively</u> for the <u>whole</u> of the silver and the chromate in the yellow silver-chromate gelatin systems , under various conditions.

(1) The present investigation provides further very definite evidence that supersaturation does occur.

(2) Cf. Chatterji and Dhar, J.Indian Chem.Soc., <u>5</u> (1928) 175.

In the second place it was desired to obtain a measure of the degree of supersaturation of the silver chromate and to study its dependence upon the concentration and reaction of the gelatin. Light would thus be thrown upon what may, for convenience, be called the true inhibitive action[1] of the gelatin, i.e., its power of maintaining the silver chromate in a state of supersaturation. Bolam and Mackenzie[2] found that acidification of the gelatin led to a decrease in the amount of this substance which was necessary to prevent visible change at a given concentration of silver nitrate and potassium chromate. This effect has been investigated in order to decide how far the decrease is due to change in the true inhibitive action of the gelatin, as distinct from other influences. The effect of varying the concentration of gelatin, while maintaining the p_H constant has also been studied from the same point of view. Finally a few experiments were carried out with gelatin which had been hydrolysed by heating with water.

(1) The term "inhibition value" as used in the following pages applies to the result of the combination of all the effects produced by the gelatin. In no case are the data complete enough to furnish the "true inhibition value", i.e., the minimum concentration of gelatin required to maintain a given degree of supersaturation under certain definite conditions.

(2) Bolam and Mackenzie, Trans.Farad.Soc., 22 (1926) 151.

The promotion of supersaturation by lyophilic colloids has been established in a number of other cases. Amongst the more careful investigations in this connection are those of Findlay and King[1] (carbon dioxide and various colloids, including gelatin), Langdon [2] (silver chloride and gelatin), and Bolam [3] (lead iodide and agar). The phenomenon would appear to be of general interest, apart from the problem of periodic precipitation. We may reasonably expect that its study will elucidate the processes involved in the appearance of a new phase and increase our knowledge of the characteristic properties of lyophilic colloids. It moreover must be of significance in certain biological and technical processes.

(1) Findlay and King, J.C.S., 103 (1913) 1170.

(2) Langdon, Trans.Faraday Soc., 19 (1923) 285.

(3) Bolam, Ibid., 24 (1928) 463, 26 (1930) 133.

EXPERIMENTAL

Precipitation Experiments

The gelatin used in this research was supplied by Messrs. Cox Ltd. of Edinburgh, being a sample of their highest grade of material and prepared in the same manner as the gelatin (A) used by Williams and Mackenzie [1] and that (B) employed by Bolam and Mackenzie.[2] When dried to constant weight at 105°C. it was found to contain 15.2 per cent. moisture, and on ignition to give 0.96 per cent. ash. Gelatin A contained 17.6 per cent. and gelatin B 17.65 per cent. of moisture, while the values for ash were 1.2 and 1.0 per cent. respectively. The ash of all three samples consisted mainly of calcium oxide, a small quantity of sulphate being also present. Gelatin C proved to be more susceptible to bacteriological action than either A or B and the precaution was taken of using only freshly prepared solutions.

A.R. silver nitrate, potassium chromate, ammonium nitrate, sodium hydroxide, and Kahlbaum's acetic acid were employed, and all solutions were prepared from particularly good distilled water.

The procedure adopted for ascertaining the amount of gelatin required to prevent precipitation in mixtures of silver nitrate and potassium chromate was essentially that of Williams and Mackenzie and

(1) Williams & Mackenzie, J.C.S., 117 (1920) 844.
(2) Bolam & Mackenzie, Trans.Farad.Soc., 22 (1926) 151.

Bolam and Mackenzie. In each of one series of Pyrex test-tubes were placed 5 c.c. of xN. silver nitrate, and in each of another series 5 c.c. of xN. potassium chromate. Increasing volumes (y.c.c.) of z per cent. of (moist) gelatin solution[1] were now added to successive tubes in the two series and the contents of corresponding tubes thoroughly mixed by first pouring the silver nitrate into the potassium chromate and then transferring the liquid from one tube to the other five or six times. Immediately after mixing (during which the solutions were kept at a temperature of approximately 25°C.) the tubes containing the mixtures were tightly corked and placed in a thermostat maintained at 25°C. $\pm$0.1°C. by electrical regulation, and carefully examined after a period of 72 hours. To avoid the reduction of the silver salt by the gelatin which takes place on exposure to light, the tubes were screened from the latter. In all cases where change occurred, either a light red precipitate appeared in the body of the mixture (general precipitation) and proceeded to settle out, provided the gelatin was still liquid, or else darker patches of silver chromate formed on the side of the tube. No large black crystals were observed at the relatively high concentrations investigated, which agrees with previous experience. (See Williams and Mackenzie and Bolam and Mackenzie).

(1) The gelatin was dispersed at 35°C. and the solution used immediately.

From the above it will be seen that the composition of any mixture can be represented by,

5 c.c. xN.$AgNO_3$ + y c.c. z per cent. gelatin + 5 c.c. xN.K_2CrO_4 + y c.c. z per cent. gelatin.

In a given series there will be a value for y, which we may call y^*, at which any visible change is just inhibited. The concentration of gelatin (dry) is evidently given by,

$$\frac{2y^*}{10 + 2y^*} \times z \times \frac{100 - 15.2}{100} \text{ per cent.}$$

and may be termed the "inhibition value" of the gelatin for the particular concentration of silver chromate present, this being equal to

$$\frac{5}{10 + 2y^*} \times \frac{x}{2} \times 1{,}000 \text{ millimols per litre.}$$

To ensure reasonable reproducibility of the results, the tubes were thoroughly cleaned before each experiment with hot water, nitric acid, and ammonia, steamed out and dried in an air oven. Care was taken to avoid scratching the internal surface of the tubes during the cleaning operations, since precipitation tended to take place more readily on the scratches than elsewhere.

A series of inhibition values were obtained

for gelatin at each of the following p_H values - 5.7, 5.3, 5.0, 4.8 - 4.9, 4.7, 4.3. P_H values were determined colorimetrically, using the sodium acetate-acetic acid mixtures of Walpole as standards. Methyl red was selected as indicator except in the case of p_H = 4.3, where B.D.H. "Universal" indicator was found to be the most satisfactory. A one per cent. solution of gelatin C was found to have a p_H value of 5.3 and the p_H was raised or lowered by the addition of sodium hydroxide or acetic acid respectively. The following indicates the method employed in adjusting the p_H. Into each of a series of uniform flat-bottomed cylindrical tubes were placed 10 c.c. of 1 per cent. gelatin solution and 2 drops of indicator. Increasing known amounts of 0.1 N acetic acid were added to successive tubes and comparison made with standards lying 0.1 of a p_H on opposite sides of the desired value. In this manner the proportion of acetic acid to be added to a given amount of gelatin was estimated with sufficient accuracy, as was shown by checking the p_H of the solutions actually used for the precipitation experiments.

The results obtained are given in detail in Table I, from which the degree of precision attained will be realised. The interpretation of the symbols

is as follows,

+	=	general precipitation
(+)	=	precipitation on side of tube
((+))	=	trace of precipitation on side of tube
-	=	no change, mixture remaining clear and yellow.
*	=	precipitation just inhibited.

Only the observations in the neighbourhood of the inhibition point are recorded. In every case mixtures with a smaller value for y than those shown in the table gave general precipitation whereas mixtures with a larger value exhibited no change.

In Table II are collected the inhibition values calculated from the y^* values in the manner already explained. The figures in the last two columns are also plotted against each other in Fig.4, page 68. I am indebted to Miss J.G.Ogilvie, B.Sc., for the inhibition values for gelatin of $p_H = 5.3$.

TABLE I.

Precipitation experiments

p_H	x ($\times 10^2$)	z	y	1	2	3	4
5.7	0.67	1.0	5.4		+		
			5.6		+		
			5.8	+	(+)		
			6.0*		-		
			6.2	-	-		
			6.4	-	-		
	1.0	3.0	5.0	+	+		
			5.2	+	+		
			5.4	(+)	-		
			5.6*	-	-		
			5.8	-	-		
			6.0	-	-		
	2.0	6.0	7.8	+	+		
			8.0	+	+	+	+
			8.2	+	(+)	+	+
			8.4			(+)	(+)
			8.5*				
			8.6				-
5.3	0.25	0.50	1.4	+	+	+	+
			1.45	+		+	+
			1.50*	+	-	-	-
			1.55	+		-	-
			1.60	-	-	-	-
	0.33	1.0	1.6	+	+	+	+
			1.7	-	+	+	+
			1.75		+	+	+
			1.8*	-	-	-	+
			1.85		-	-	-
			2.0	-			
	0.50	2.0	2.0	+	+	+	+
			2.1	(+)	-	+	+
			2.15*				
			2.2	-	-	-	-

TABLE I. (continued)

p_H	x (×10²)	z	y	1	2	3	4
5.3	0.80	2.5	3.5	+	+	+	+
			3.6	-	+	+	+
			3.7*		-	-	+
			3.8		-	-	-
	1.0	3.0	4.4	+	+	+	+
			4.5	-	+	+	+
			4.6*	(+)	(+)	-	-
			4.7	-	-	-	-
	1.25	4.0	4.8	+	+	+	+
			4.9		+	+	+
			5.0*	-	(+)	(+)	+
			5.1		-	-	-
	1.67	5.0	6.2	+	+	+	
			6.3	-	+	+	
			6.4*	-	(+)	-	+
			6.7	-	-		-
5.0	1.0	1.0	6.1	(+)	+	+	
			6.3	+	+	+	
			6.5	(+)	+	+	
			6.7	-	+	-	
			6.8*				
			6.9	-	-	-	
	2.0	2.0	10.5	+	+		
			10.8	+	+		
			11.1	(+)	+		
			11.4	-	(+)		
			11.7*	(+)	(+)?		
	2.0	6.0	5.6	+	+	+	
			5.8	+	+	(+)	
			6.0*	(+)	(+)	-	
			6.2	-	-	-	

TABLE I (continued)

p_H	x ($\times 10^2$)	z	y	1	2	3	4
4.8-4.9	1.0	1.0	5.9		+		
			6.1	+	+		
			6.3*		-		
			6.5	-	-		
	2.0	2.0	10.2				+
			10.4	+			
			10.5				+
			10.8*			-	-
			11.1	+		-	-
			11.2		-		
			11.4		-	-	
4.7	0.33	0.20	2.5	+			
			2.8		+		
			3.0	+	+		
			3.2*		-		
			3.4		-		
			3.5	-			
	1.0	1.0	4.4		+	+	
			4.6		+	+	
			4.8*	-	-	-	
			5.0	-	-	-	-
			5.2	-	-	-	-
	1.33	3.0	3.8			+	
			4.0			+	
			4.2	+	-	-	
			4.4*		-	-	
			4.6			-	
	2.0	6.0	4.6	+	+		
			4.8	+			
			5.0*		-		
			5.2				
			5.4		-	-	

TABLE I (Continued)

p_H	x ($\times 10^2$)	z	y	1	2	3	4
4.3	1.0	1.0	2.6	+			
			2.8		+		
			3.0	+		-	-
			3.1*				
			3.2			-	-
			3.4	-		-	-
	1.33	3.0	2.4	+	+		
			2.6	+	+	+	+
			2.7			+	+
			2.8*	-		-	
			3.0	-			
	1.54	5.0	2.2				
			2.4		+		
			2.5			+	+
			2.6		-		
			2.7*		-	-	
			2.8	-	-		

TABLE II

"Inhibition values" of gelatin at 25°C.

p_H of gelatin.	x	z	y*	Conc. of Ag_2CrO_4 (millimols per litre)	"Inhibition value" of gelatin.
5.7	0.0067	1.0	6.0	0.76	0.46
	0.010	3.0	5.6	1.18	1.34
	0.020	6.0	8.5	1.85	3.20
5.3	0.0025	0.50	1.5	0.48	0.10
	0.0033	1.0	1.8	0.62	0.22
	0.0050	2.0	2.15	0.88	0.51
	0.0080	2.5	3.7	1.15	0.90
	0.010	3.0	4.6	1.30	1.22
	0.0125	4.0	5.0	1.57	1.69
	0.0167	5.0	6.4	1.83	2.38
5.0	0.010	1.0	6.8	1.06	0.49
	0.020	2.0	11.7	1.50	1.18
	0.020	6.0	6.0	2.28	2.77
4.8-4.9	0.010	1.0	6.3	1.11	0.47
	0.020	2.0	10.8	1.58	1.16
4.7	0.0033	0.20	3.2	0.51	0.07
	0.010	1.0	4.8	1.28	0.42
	0.0133	3.0	4.4	1.78	1.19
	0.020	6.0	5.0	2.41	2.54
4.3	0.010	1.0	3.1	1.55	0.32
	0.0133	3.0	2.8	2.14	0.91
	0.0154	5.0	2.7	2.50	1.49

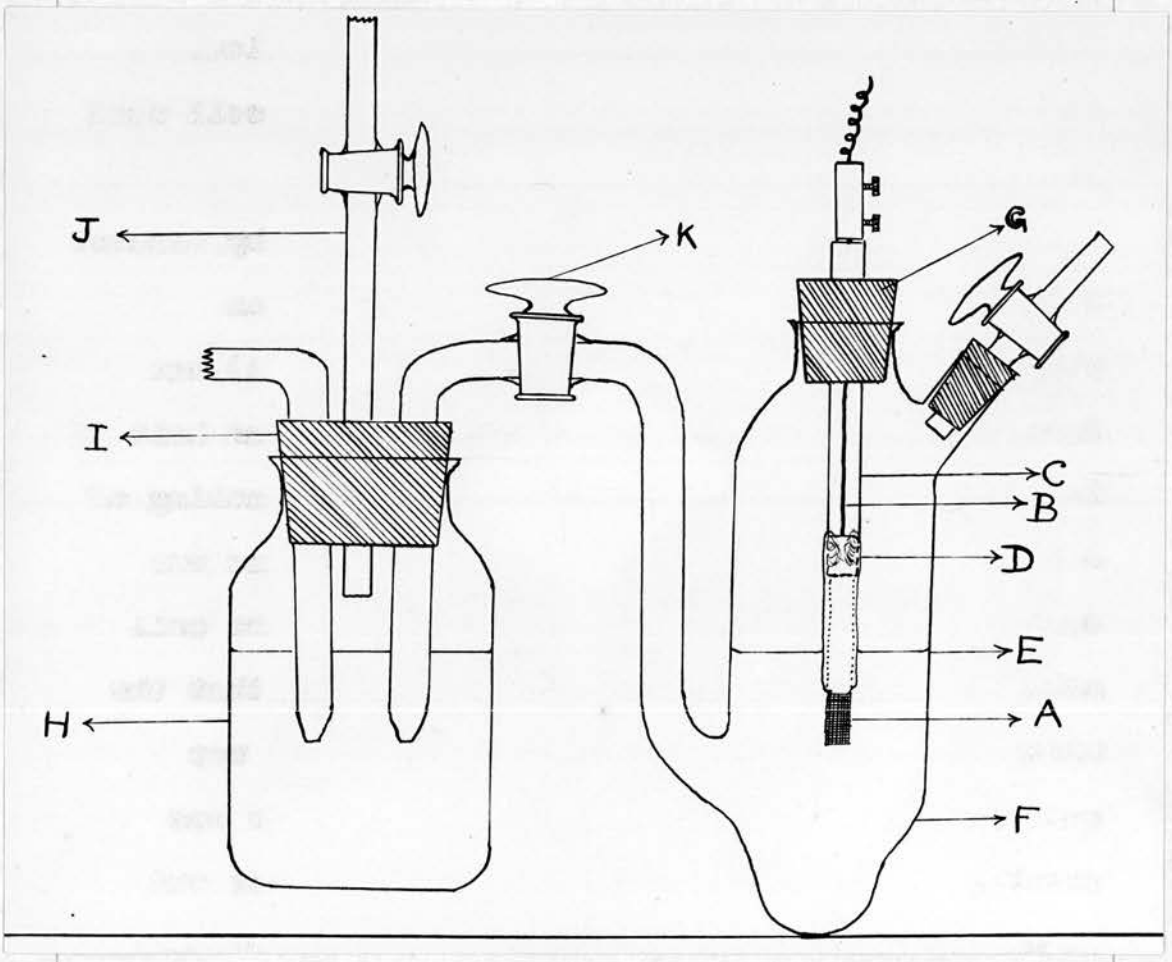

Fig. 1.

E.m.f. Measurements.

The activity of the silver ion in the various systems was obtained by measurement of the e.m.f. of a concentration cell of the type

Ag, 0.1 M $AgNO_3$, 10 M. NH_4NO_3, S, Ag,

where S denotes the system under investigation. Fig. 1 illustrates the construction of the cell used in the great majority of the experiments.

Fine pure silver gauze (supplied by Messrs. Johnson, Matthey and Co., London) was used as electrode material. A strip of the gauze (A) was fused to a piece of stout copper wire (B) and held in position in a glass tube (C) by a firm packing of cotton-wool (D). The upper part of the gauze was coated with paraffin wax and the level of the cell solution (E) was always adjusted to ensure that the unwaxed portion (about 1 c.m. from the tip) was entirely immersed. Before use the electrode was carefully annealed by heating to dull redness and quenching in cold water. Entirely new electrodes were prepared for each experiment. By adopting the above precautions it was found possible to obtain results which compared favourably with those given by silver plated platinum or silver gauze electrodes. Plated electrodes proved to be much less convenient

for the investigation of the gelatin systems than those consisting simply of the massive metal.

The electrode was held in position in a half-cell (F) of the usual type by means of a rubber stopper (G). Connection between the two sides of the cell was effected by means of the ammonium nitrate solution contained in a wide-mouthed bottle (H), closed by a three-holed rubber stopper (I), through which passed the siphons of the half-cells and also a glass tube bearing a tap (J). With the tap open, the tube allowed for displacement of the connecting liquid when the half-cell siphons were pushed into position. Closing of the tap after the cell had reached thermal equilibrium ensured that no ammonium nitrate would pass over into the electrode chambers when the siphon taps (K and L) were opened. The cell was placed in a thermostat regulated to vary from 25.0°C. by not more than 0.1°C.

The ordinary potentiometric method of determining the e.m.f. was employed. Two similar resistance boxes (Gambrell's Class B: accuracy = 1 in 1,000) joined in series to give a total resistance of 11,110 ohms were used instead of a bridge-wire, the null-point being found by varying the ratio between them. An "Onwood" galvanometer

by Gambrell was used as null-point instrument. The Pye standard cadmium cell was checked at intervals against a second standard certified by the National Physical Laboratory as giving an e.m.f. of 1.01835 volts at 15°C.

Potentials in pure solutions of silver nitrate. - In order to arrive at a basis for the interpretation of the data obtained for the gelatin systems, it was necessary to investigate the behaviour of the electrodes in some simple aqueous systems. A series of determinations were therefore made of the e.m.f. values given by cells of the general type described above, in which the right hand side (S) consisted of a pure aqueous solution of silver nitrate. The data are given in Table III, where the concentration of this solution is shown in the first column. The table gives the value of the e.m.f. for intervals of half an hour and one hour after placing the cell in the thermostat. Each pair of values represents entirely fresh electrodes. It will be seen that the potential changed during the interval between the two readings seldom by more than 0.4 of a millivolt and usually by less, and also that in any given series of determinations the maximum variation from

the mean of the half-hour values was about 1.0 millivolt.

The e.m.f. values shown in the last column of Table III were calculated from the formula

$$\text{E.m.f.} = 0.0591 \log \frac{(a_{Ag^+})_1}{(a_{Ag^+})_2}$$

(where $(a_{Ag^+})_1$ and $(a_{Ag^+})_2$ represent the activity of the silver ion in 0.1 M $AgNO_3$ and in the solution of variable concentration of $AgNO_3$, respectively) by means of the activity coefficients suggested by Lewis and Randall. (see Table IV). It will be seen that the experimental e.m.f. values were uniformly lower than those calculated.

TABLE III

E.m.f. values for aqueous silver nitrate concentration cells at 25°C.

Conc. of $AgNO_3$ (millimols per litre)	E.m.f. (millivolts)			
	Half-hour reading.	One hour reading.	Mean*	Calculated.
1.0	109.9 111.8 111.4 110.7	109.9 111.4 111.4 110.4	111.0	112.3
1.25	105.4 105.0	104.2 105.2	105.2	106.6
1.50	101.0 100.4 101.3 101.1	101.3 100.4 101.5 101.5	101.0	102.0
2.0	92.5 92.3	92.8 92.3	92.4	94.7
3.33	80.8 80.4	80.8 81.0	80.6	82.0
4.0	72.4 74.0 73.3	73.3 74.0 72.9	73.2	77.5
10.0	53.8 54.0 53.6 54.5 53.7 53.8	53.7 54.0 53.7 54.0 53.8 53.8	53.9.	55.1

* Mean of half-hour readings.

TABLE IV

Lewis and Randall's values for a_{Ag^+} in aqueous silver nitrate solutions.

Conc. of $AgNO_3$ (millimols per litre)	Activity coefficient.	a_{Ag^+} ($\times 10^3$)	$-\log a_{Ag^+}$
1.0	0.970	0.97	3.013
1.25	0.968	1.21	2.917
1.50	0.965	1.45	2.839
2.0	0.960	1.92	2.717
3.33	0.947	3.15	2.502
4.0	0.940	3.76	2.425
10.0	0.770	77.0	1.114

Potentials in "critical mixtures" of gelatin, silver nitrate, and potassium chromate. - By "critical mixture" is meant a mixture in which visible change within 72 hours was just prevented, i.e., a mixture in which the concentration of gelatin was equal to its inhibition value for the concentration of silver chromate present. In every case the right hand side of the cell (S) consisted of one of the mixtures whose composition is given in the last two columns of Table II, p.18

Table V contains the whole of the results, except for a few experiments in which the e.m.f. changed by more than 1.0 millivolt between the half-hour and hour readings. More often than not the change was considerably less than 0.1 millivolt. No complete explanation can be given for the cases of exceptionally rapid change, but it was usually found to occur with electrodes which gave values greater than 54.4 millivolts and less than 53.2 millivolts when tested in a 0.1 M $AgNO_3$ - 0.01 M $AgNO_3$ concentration cell, prior to the measurement in the gelatin system. All the electrodes used for the experiments with gelatin of p_H = 5.3 in Table V (and Table VI) were so tested and found to conform to the above limits.

In Table V and succeeding tables, the e.m.f. values given are all half-hour values.

TABLE V

E.m.f. values for "critical mixtures" of silver nitrate, potassium chromate and gelatin at 25°C.

p_H of gelatin.	Conc. of Ag_2CrO_4 (millimols per litre)	Conc. of gelatin. (per cent)	E.m.f. (millivolts)	
			Half-hour reading.	Mean.
5.7	0.76	0.46	112.2 112.2 110.4	111.6
	1.18	1.34	107.0 108.8 108.8	108.2
	1.85	3.20	109.6 110.5 109.6	109.9
5.3	0.48	0.10	116.3 116.1 117.3	116.6
	0.62	0.22	112.0 112.3 115.0 113.6	113.2
	0.88	0.51	107.2 107.5 109.9 110.9 108.1 108.7	108.7

TABLE V (continued)

p_H of gelatin.	Conc. of Ag_2CrO_4 (millimols per litre)	Conc. of gelatin. (per cent)	E.m.f. (millivolts)	
			Half-hour reading.	Mean.
5.3	1.15	0.90	105.0 104.3 104.9	104.7
	1.30	1.22	105.2 103.6 105.2 103.4 104.5	104.3
	1.39	1.37	103.4 102.0 105.8 103.7 105.5	104.1
	1.45	1.48	103.9 104.7 103.0	103.9
	1.57	1.69	103.5 105.9 104.1 104.4 103.1	104.2
	1.68	1.97	103.1 105.2 102.3 103.5 105.2	103.9

TABLE V (Continued)

p_H of gelatin.	Conc. of Ag_2CrO_4 (millimols per litre)	Conc. of gelatin. (per cent)	E.m.f. (millivolts)	
			Half-hour reading.	Mean
5.3	1.83	2.38	103.8 103.8 104.4 103.5	103.9
5.0	1.06	0.49	100.1 99.5 100.1	99.9
	1.50	1.18	95.0 95.9 97.3	96.1
	2.28	2.77	93.1 94.0 93.1	93.4
4.8-4.9	1.11	0.47	99.9 100.6 98.7	99.7
	1.58	1.16	94.1 94.5 93.6	94.1
4.7	0.51	0.07	113.2 113.2 112.4	112.9

TABLE V (Continued)

p_H of gelatin.	Conc. of Ag_2CrO_4 (millimols per litre)	Conc. of gelatin. (per cent)	E.m.f. (millivolts)	
			Half-hour reading.	Mean
4.7	1.28	0.42	97.2 96.6 95.9	96.6
	1.78	1.19	92.3 93.2 91.4	92.3
	2.41	2.54	86.7 86.2 85.8	86.2
4.3	1.55	0.32	87.2 89.0 88.1	88.1
	2.14	0.91	79.9 81.7 81.7	81.1
	2.50	1.49	73.5 76.2 75.3	75.0

Potentials in mixtures of silver nitrate and gelatin. - In order to ascertain the influence of the gelatin alone on the activity of the silver ion in solutions of silver nitrate, a study was made of the silver potentials in mixtures of silver nitrate and gelatin of $p_H = 5.3$. The systems actually examined differed from those at the same p_H given in Table V, p. 27, only in that potassium chromate was absent. They were also prepared in the same way so that their composition may be represented by,

5 c.c. x N $AgNO_3$ + y c.c. z per cent.gelatin(moist)
+ 5 c.c. water + y c.c. z per cent.gelatin(moist)

(see p. 11). Table VI contains the data for these experiments. The degree of constancy and of reproducibility of e.m.f. was found to be the same as in the case of the critical mixtures.

TABLE VI

E.m.f. values for mixtures of silver nitrate and gelatin (p_H = 5.3) at 25°C.

Conc. of $AgNO_3$ (millimols per litre)	Conc. of gelatin (per cent)	E.m.f. (millivolts)	
		Half-hour reading.	Mean
0.96	0.10	116.7 117.8 117.3 117.5	117.3
1.75	0.51	108.1 111.9 111.9 111.0 110.5 111.3 110.4 108.2 107.7	110.1
2.60	1.22	101.6 103.1 103.7 105.3	103.4
2.78	1.37	105.4 102.4	103.9
3.13	1.69	103.4 104.7	104.1
3.65	2.38	104.3 102.4 105.5	104.0

Potentials in "equilibrium mixtures" of silver chromate, Potassium chromate and gelatin. - The object of the experiments described in this section was to determine the potentials developed in mixtures of potassium chromate and gelatin which were saturated with respect to silver chromate. Saturation was attained by shaking the mixture with solid silver chromate for a suitable length of time at constant temperature. Under these conditions silver chromate dissolved in the mixture until a state of equilibrium between silver, chromate and gelatin was reached. The resulting system may therefore be called an "equilibrium mixture" to distinguish it from a "critical mixture" in which there is every reason to believe that silver chromate is present in supersaturated solution.

Silver chromate was prepared by the interaction of pure aqueous solutions of silver nitrate and potassium chromate. The precipitate was thoroughly washed with distilled water and dried in an air oven. A quantity of the solid was placed with the solution of potassium chromate and gelatin in a resistance-glass bottle and the mixture well shaken for five hours in a thermostat maintained at 25°C. $\pm$ 0.1°C. The e.m.f. was then determined by means of a cell of the type already described.

It was necessary to make certain that the shaking period of five hours was sufficient to saturate the solutions with silver chromate and a number of experiments were carried out to test this. In the first place silver chromate was shaken with a solution of 0.01 M potassium nitrate, the latter being present to provide a satisfactory null-point, for 4 hours in one case, and 18 hours in another. The results are given in Table VII and it will be observed that no significant difference exists between the two sets of figures. A second series of experiments in which the silver chromate was shaken with 0.85 per cent. gelatin solution for periods of 4 and 18 hours showed similar agreement (see Table VIII).

The final test was made with a mixture of 1.69 per cent. gelatin and 1.19 millimols per litre potassium chromate. In addition to results for 5 hours and 11 hours shaking, further figures were obtained in the following manner. A portion of the mixture after shaking for 5 hours was sucked up into a tube just wide enough to take the electrode and allowed to stand at 25.0°C. The liquid soon gelled and the large amount of silver chromate which had been added remained dispersed throughout the mass. After three days an electrode was inserted in the

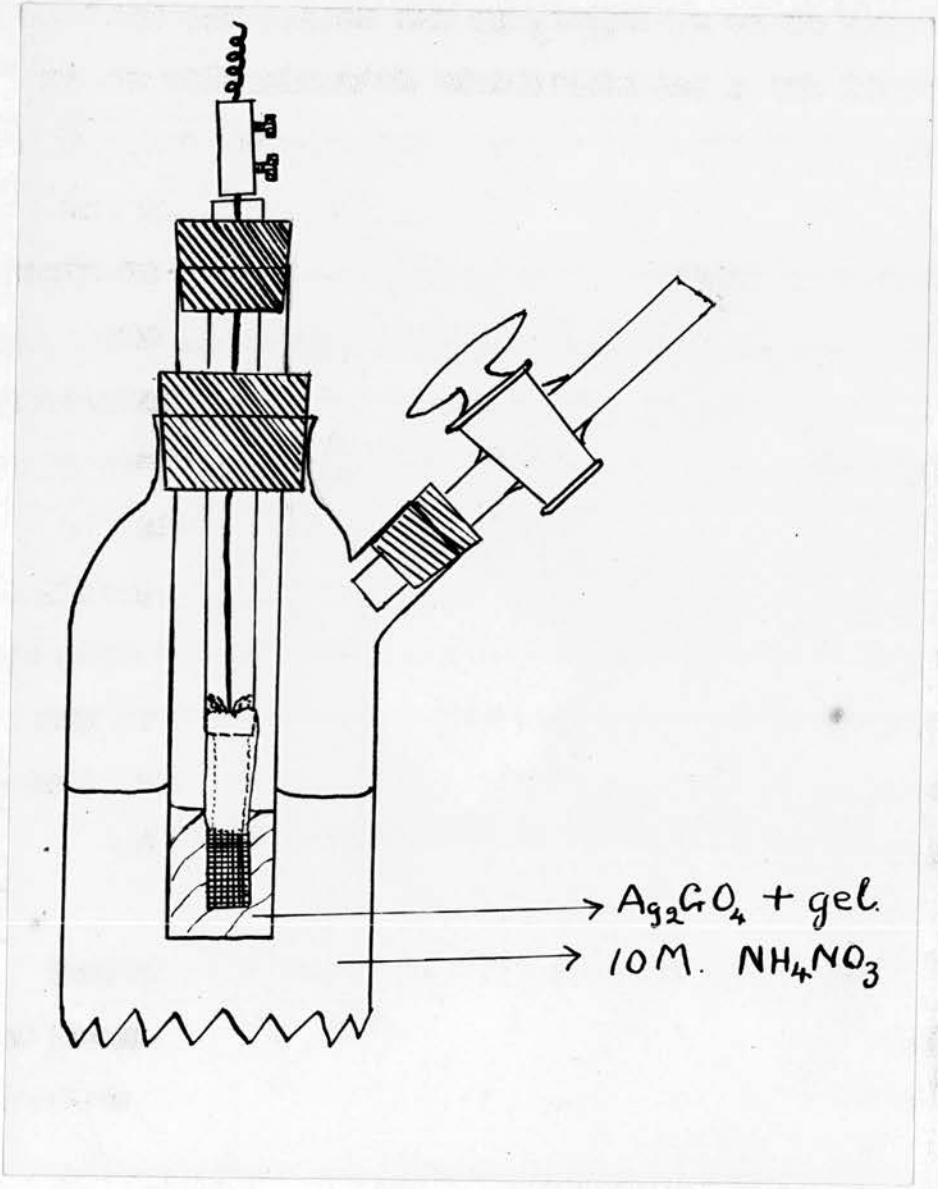

Fig. 2.

gel and the tube fixed by means of a rubber stopper in the neck of a half-cell vessel (see Fig.2) so that the lower end of the gel made contact with a quantity of 10 M. NH_4NO_3 in the cell. The half-cell arranged for a potentiometric determination as in Fig.1. A similar experiment was carried out with a portion of the mixture which had been shaken for 11 hours; in this case the gel was allowed to stand for 2 days after the shaking. The results are tabulated in Table IX. The first two experiments clearly establish that shaking for 5 hours was just as effective as shaking for 11 hours. While the figures for the last two experiments are appreciably lower than the others, the difference still does not exceed the possible experimental error. Thus the conclusion may be drawn from the whole series that shaking for 5 hours was sufficiently close to saturation for the present purpose.

Saturation of a mixture of gelatin and potassium chromate with silver chromate produced an unknown increase in the total concentration of chromate. The amount of silver chromate which had dissolved was found by measurement of the e.m.f. in systems containing the same amount of gelatin and potassium chromate[1] as the equilibrium system and also known amounts of

(1) For conductivity only; has no effect on actual e.m.f.

silver nitrate. That concentration of silver nitrate which gave the same e.m.f. as the equilibrium mixture could be taken as equal to the concentration of silver in the latter.

Now it was desired to obtain e.m.f. values for equilibrium mixtures which were identical in respect to gelatin and total chromate content with the critical mixtures which had been investigated. The following example illustrates the method adopted.

Composition of critical mixture :-

Gelatin (p_H = 4.3) = 0.91 per cent.
Silver nitrate = 4.27 millimols per litre
Potassium chromate = 2.14 millimols per litre.

(A) E.m.f. values in equilibrium mixtures containing 0.91 per cent. gelatin (p_H = 4.3) and potassium chromate at various concentrations :-

	I	II	III
Millimols K_2CrO_4 per litre(c)	1.61	1.89	2.47
E.m.f (E)	124.6	131.7	137.7

(B) E.m.f. values for mixtures of 0.91 per cent. gelatin (p_H = 4.3) + 2.14 millimols per litre potassium chromate + silver nitrate at various concentrations :-

Millimols $AgNO_3$ per litre (m)	0.86	0.59	0.46
E.m.f. (E)	121.5	133.8	139.0

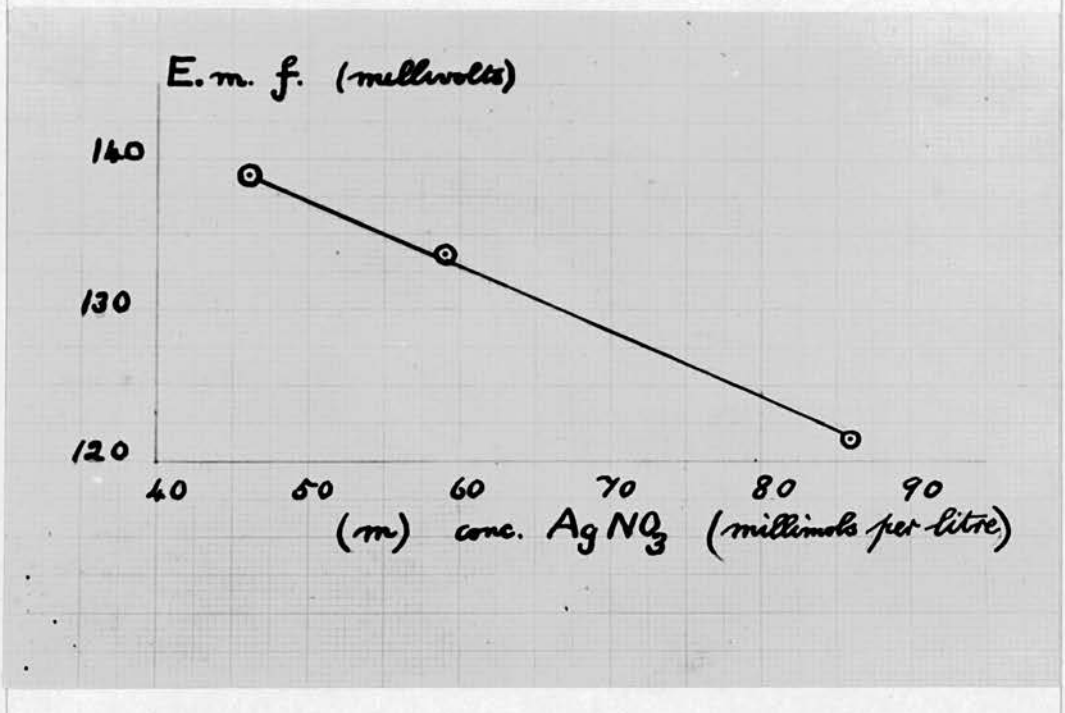
E. m. f. (millivolts)
140
130
120
40
50
60
70
80
90
(m) conc. $AgNO_3$ (millimols per litre)

Fig. 3.

Plotting m against E the accompanying graph is obtained (see opposite page). From this graph are derived the following values of m, corresponding to the values of E given by the equilibrium mixtures.

System	E.	m.
I	124.6	0.80
II	131.7	0.62
III	137.7	0.48

It is evident that the total chromate concentrations in the equilibrium systems are given by :-

$$\text{Total chromate} = c + \frac{m}{2} \text{ millimols per litre.}$$

The actual values are shown below,

System	c.	m	$c + \frac{m}{2}$
I	1.61	0.80	2.01
II	1.89	0.62	2.20
III	2.47	0.48	2.71

The final step is to derive from the above figures the e.m.f. corresponding to a total chromate concentration of 2.14 millimols per litre, which is the concentration in the given critical mixture. Collecting

together the values for total chromate and e.m.f. we have :-

System	Total chromate	E.
I	2.01	124.6
II	2.20	131.7
III	2.71	137.7

In view of these figures and of the possible uncertainty in the potential measurements, (about 2.0 millivolts in the case of the equilibrium systems) it may be assumed that the e.m.f. changes by 0.22 millivolts when the total chromate changes by 0.01. This gives the value of 130.6 millivolts for the e.m.f. in the case of the equilibrium system containing 2.14 millimols of chromate per litre.

The results of these experiments are given in Tables (10a - 10p). Each table shows the complete data obtained in determining the e.m.f. for the equilibrium system corresponding to a particular critical system, Sections A and B of the table are as described in the above example. In Section C are brought together the figures necessary for the final calculation, viz., the concentrations of potassium

chromate (c.), silver chromate (m) (derived from Section B, as described above), total chromate ($c + \frac{m}{2}$), and the corresponding e.m.f. values (from Section A). The table concludes with the required e.m.f. value, calculated from the last two columns in Section C (also as above).

TABLE VII

E.m.f. values for 0.01 M potassium nitrate saturated with silver chromate at 25.0°C.

Period of shaking.	E.m.f. (millivolts)			
	½ hr. reading.	1 hr. reading.	22 hrs. reading.	Mean*
4 hrs.	147.3 147.3 148.2	147.3 147.5 147.5	148.1 148.9 146.1	147.6
			19 hrs. reading.	
18 hrs.	148.7 148.4 148.9	147.3 147.5 147.3	148.1 148.9 146.1	148.7

TABLE VIII

E.m.f. values for 0.85 per cent.gelatin (p_H= 5.3) saturated with silver chromate at 25.0°C.

Period of shaking.	E.m.f. (millivolts)			
	½ hr. reading.	1 hr. reading.	19 hrs. reading.	Mean*
5 hrs.	143.0 144.8 144.0	145.2 144.5 145.2	(140.3) 143.0 144.0	143.9
18 hrs.	144.0 144.7 144.7	144.9 144.7 144.7	- - -	144.5

* Mean of half-hour readings.

TABLE IX

E.m.f. values for mixture of 1.69 per cent. gelatin (p_H = 5.3) and 1.19 millimols per litre potassium chromate saturated with silver chromate at 25.0°C.

Procedure.	E.m.f. (millivolts)			
	Half-hour reading.	One hour reading.	20 hrs. reading	Mean*
5 hours shaking.	165.8 165.8 165.8	165.4 165.8 165.2	165.0 165.0 165.2	165.8
11 hours shaking.	165.4 166.3	164.5 167.2	- -	165.8
			2 hours reading.	
5 hours shaking + 3 days standing.	163.5	164.2	164.4	163.7
11 hours shaking + 2 days standing.	163.9	163.0	-	

* Mean of half-hour reading.

TABLE X a.

p_H = 5.7. Conc. gelatin = 0.46 per cent.

A

Conc. K_2CrO_4 (millimols per litre)	E.m.f. (millivolts)	Mean
0.46	164.8 164.8 166.6	165.4
0.67	168.6 169.4 168.6	168.9

B

Conc. $AgNO_3$ (millimols per litre)	E.m.f. (millivolts)	Mean
0.23	180.4 181.3 179.5	180.4
0.28	175.6 174.8 175.6	175.3
0.45	155.7 153.8 153.8	154.5

C

Conc. CrO_4 as K_2CrO_4	Conc. CrO_4 as Ag_2CrO_4	Total conc. CrO_4	E.m.f. (m.v.)
0.46	0.18	0.64	165.4
0.67	0.16	0.83	168.9

Hence when total chromate = 0.76 millimols per litre,

e.m.f. = 167.6 millivolts.

TABLE X b.

p_H = 5.7. Conc. gelatin = 1.34 per cent.

A

Conc. K_2CrO_4 (millimols per litre)	E.m.f. (millivolts)	Mean
0.79	169.7 168.8	169.3
0.95	172.3 172.3 172.3	172.3

B

Conc. $AgNO_3$ (millimols per litre)	E.m.f. (millivolts)	Mean
0.47	188.1 188.1 188.1	188.1
0.59	178.7 178.7 179.7	179.0
0.86	162.9 163.9 165.9	164.2

C

Conc. CrO_4 as K_2CrO_4	Conc. CrO_4 as Ag_2CrO_4	Total conc. CrO_4	E.m.f. (m.v.)
0.79	0. 38	1. 17	169.3
0.95	0. 35	1. 30	172.3

Hence when total conc. CrO_4 = 1.18 millimols per litre,

e.m.f. = 169.4 millivolts.

TABLE X c.

p_H = 5.3. Conc.gelatin = 0.10 per cent.

A

Conc. K_2CrO_4 (millimols per litre)	E.m.f. (millivolts)	Mean
0.41	166.5 166.5 166.5	166.5
0.48	167.4 169.2 165.6	167.4

B

Conc. $AgNO_3$ (millimols per litre)	E.m.f. (millivolts)	Mean
0.16	169.6 168.7 167.8	168.7
0.19	165.6 164.7 163.8	164.7
0.24	160.1 159.2 160.1	159.8

C

Conc. CrO_4 as K_2CrO_4	Conc. CrO_4 as Ag_2CrO_4	Total conc. CrO_4	E.m.f. (m.v.)
0.41	0.09	0.50	166.5
0.48	0.985	0.565	167.4

Hence when total conc. CrO_4 = 0.48 millimols per litre,

e.m.f. = 166.3 millivolts.

TABLE X d.

p_H = 5.3. Conc.gelatin = 0.51 per cent.

A

Conc. K_2CrO_4 (millimols per litre)	E.m.f. (millivolts)	Mean
0.70	165.0 165.0 166.8	165.6
0.88	168.5 168.5 170.1	169.0

B

Conc. $AgNO_3$ (millimols per litre)	E.m.f. (millivolts)	Mean
0.35	167.7 169.2 167.7	168.2
0.39	165.9 164.9 166.4	165.7

C

Conc. CrO_4 as K_2CrO_4	Conc. CrO_4 as Ag_2CrO_4	Total conc. CrO_4	E.m.f. (m.v.)
0.70	0.20	0.90	165.6
0.88	0.17	1.05	169.0

Hence when total conc. CrO_4 = 0.88 millimols per litre,

e.m.f. = 165.1 millivolts.

TABLE X e.

p_H = 5.3. Conc.gelatin = 1.22 per cent.

A

Conc. K_2CrO_4 (millimols per litre)	E.m.f. (millivolts)	Mean
1.00	165.9 166.5 166.6	166.3
1.09	166.9 166.5 166.4	166.6
1.30	167.6 166.8 167.6	167.3
1.45	171.5 170.9 171.5	171.3

B

Conc. $AgNO_3$ (millimols per litre)	E.m.f. (millivolts)	Mean
0.52	171.4 171.4 170.8	171.2
0.65	165.2 163.7 163.7	164.2

C

Conc. CrO_4 as K_2CrO_4	Conc. CrO_4 as Ag_2CrO_4	Total conc. CrO_4	E.m.f. (m.v.)
1.00	0. 30	1. 30	166.3
1.09	0. 30	1. 39	166.6
1.30	0. 30	1. 60	167.3
1.45	0. 26	1. 71	171.3

Hence when total conc.CrO_4 = 1.30 millimols per litre,
e.m.f. = 166.3 millivolts.

TABLE X f.

pH = 5.3. Conc. gelatin = 1.69 per cent.

A

Conc. K_2CrO_4 (millimols per litre)	E.m.f. (millivolts)	Mean
1.19	165.8 165.8 165.8	165.8
1.39	167.3 167.7 166.7 168.2 167.3 167.7	167.5
1.57	174.1 174.1 174.1	174.1

B

Conc. $AgNO_3$ (millimols per litre)	E.m.f. (millivolts)	Mean
0.50	182.0 182.9 183.9	182.9
0.63	175.6 176.0 173.4	175.0
0.83	164.0 164.0 163.5 165.9 166.6 166.6	165.1

C

Conc. CrO_4 as K_2CrO_4	Conc. CrO_4 as Ag_2CrO_4	Total conc. CrO_4	E.m.f. (m.v.)
1.19	0.41	1.60	165.8
1.39	0.39	1.78	167.5
1.57	0.33	1.90	174.1

Hence when total conc. CrO_4 = 1.57 millimols per litre,

e.m.f. = 165.0 millivolts.

TABLE X g.

p_H = 5.0. Conc. gelatin = 0.49 per cent.

A

Conc. K_2CrO_4 (millimols per litre)	E.m.f. (millivolts)	Mean
0.69	159.0 157.1 157.1	157.7
0.85	161.6 162.6 162.6	162.3
0.92	163.1 166.7 164.9	164.9

B

Conc. $AgNO_3$ (millimols per litre)	E.m.f. (millivolts)	Mean
0.35	162.2 163.1 164.9 160.8 164.4 162.7	163.0
0.42	152.5 154.4 155.2	154.0

C

Conc. CrO_4 as K_2CrO_4	Conc. CrO_4 as Ag_2CrO_4	Total conc. CrO_4	E.m.f. (m.v.)
0.69	0.20	0.89	157.7
0.85	0.18	1.03	162.3
0.92	0.17	1.09	164.9

Hence when total conc. CrO_4 = 1.06 millimols per litre,

e.m.f. = 163.3 millivolts.

TABLE X h.

p_H = 5.0. Conc.gelatin = 1.18 per cent.

A

Conc. K_2CrO_4 (millimols per litre)	E.m.f. (millivolts)	Mean
1.00	153.4 157.0 155.2	155.2
1.25	155.2 157.0 155.2	155.8

B

Conc. $AgNO_3$ (millimols per litre)	E.m.f. (millivolts)	Mean
0.50	164.4 166.2 168.0	166.2
0.62	158.9 157.0 155.2	157.0
0.75	149.4 151.2 149.4	150.0

C

Conc. CrO_4 as K_2CrO_4	Conc. CrO_4 as Ag_2CrO_4	Total conc. CrO_4	E.m.f. (m.v.)
1.00	0.33	1.33	155.2
1.25	0.32	1.57	155.8

Hence when total conc. CrO_4 = 1.50 millimols per litre,

e.m.f. = 155.6 millivolts.

TABLE X 1

p_H = 4.8 - 4.9. Conc.gelatin = 0.47 per cent.

A

Conc.K_2CrO_4 (millimols per litre)	E.m.f. (millivolts)	Mean
0.74	157.0 155.2 158.9	157.0
0.89	160.9 162.8 159.1	160.9
1.11	162.5 162.5 164.3	163.1

B

Conc. $AgNO_3$ (millimols per litre)	E.m.f. (millivolts)	Mean
0.28	162.5 163.3 164.3	163.4
0.37	157.1 159.0 157.1	157.7
0.44	152.6 151.7 151.7	152.0

C

Conc. CrO_4 as K_2CrO_4	Conc. CrO_4 as Ag_2CrO_4	Total conc. CrO_4	E.m.f. (m.v.)
0.74	0.19	0.93	157.0
0.89	0.17	1.06	160.9
1.11	0.14	1.25	163.1

Hence when total conc. CrO_4 = 1.11 millimols per litre,
e.m.f. = 161.9 millivolts.

TABLE X j.

p_H = 4.8 - 4.9. Conc.gelatin = 1.16 per cent.

A

Conc. K_2CrO_4 (millimols per litre)	E.m.f. (millivolts)	Mean
1.06	149.7 150.6 148.8	149.7
1.32	152.5 152.5 150.5	151.8
1.58	152.6 154.5 153.6	153.6

B

Conc. $AgNO_3$ (millimols per litre)	E.m.f. (millivolts)	Mean
0.66	153.9 153.9 155.7	154.5
0.79	146.2 144.4 144.4	144.9

C

Conc. CrO_4 as K_2CrO_4	Conc. CrO_4 as Ag_2CrO_4	Total conc. CrO_4	E.m.f. (m.v.)
1.06	0.36	1.40	149.7
1.32	0.35	1.67	151.8
1.58	0.34	1.92	153.6

Hence when total conc. CrO_4 = 1.58 millimols per litre,

e.m.f. = 151.1 millivolts.

TABLE X k.

p_H = 4.7. Conc. gelatin = 0.07 per cent.

A

Conc. K_2CrO_4 (millimols per litre)	E.m.f. (millivolts)	Mean
0.31	162.0 163.9 165.7	163.9
0.42	165.6 163.8 166.5	165.3

B

Conc. $AgNO_3$ (millimols per litre)	E.m.f. (millivolts)	Mean
0.17	163.9 163.9 165.8	164.5
0.20	158.4 158.4 159.3 159.2 160.1 158.2	158.9

C

Conc. CrO_4 as K_2CrO_4	Conc. CrO_4 as Ag_2CrO_4	Total conc. CrO_4	E.m.f. (m.v.)
0.31	0.09	0.40	163.9
0.42	0.085	0.505	165.3

Hence when total conc. CrO_4 = 0.51 millimols per litre,

e.m.f. = 165.3 millivolts.

TABLE X 1.

p_H = 4.7. Conc. gelatin = 0.42 per cent.

A

Conc. K_2CrO_4 (millimols per litre)	E.m.f. (millivolts)	Mean
1.02	149.9 149.9 151.8	150.5
1.22	154.2 155.2 154.6	154.7

B

Conc. $AgNO_3$ (millimols per litre)	E.m.f. (millivolts)	Mean
0.13	179.2 179.2 178.2	178.9
0.26	161.2 159.3 161.2 157.8 158.7 159.6	159.6
0.43	146.2 145.9 145.0	145.7
0.51	142.0 142.8 142.6	142.5

C

Conc. CrO_4 as K_2CrO_4	Conc. CrO_4 as Ag_2CrO_4	Total conc. CrO_4	E.m.f. (m.v.)
1.02	0.17	1.19	150.5
1.22	0.15	1.37	154.7

Hence when total conc. CrO_4 = 1.28 millimols per litre,

e.m.f. = 152.6 millivolts.

TABLE X m.

p_H = 4.7. Conc. gelatin = 1.19 per cent.

A

Conc. K_2CrO_4 (millimols per litre)	E.m.f. (millivolts)	Mean
1.33	143.0 143.0 142.0	142.7
1.78	144.7 144.7 142.9	144.1

B

Conc. $AgNO_3$ (millimols per litre)	E.m.f. (millivolts)	Mean
0.67	155.7 153.9 153.9	154.5
0.89	137.4 139.2 139.2 137.1 138.9	138.4
1.06	130.1 128.2 130.1	129.5

C

Conc. CrO_4 as K_2CrO_4	Conc. CrO_4 as Ag_2CrO_4	Total conc. CrO_4	E.m.f. (m.v.)
1.33	0.42	1.75	142.7
1.78	0.40	2.18	144.1

Hence when total conc. CrO_4 = 1.78 millimols per litre,

e.m.f. = 142.8 millivolts.

TABLE X n.

p_H = 4.3. Conc. gelatin = 0.32 per cent.

A

Conc. K_2CrO_4 (millimols per litre)	E.m.f. (millivolts)	Mean
1.03	136.3 135.4 138.1	136.6
1.37	141.8 140.9 143.5	142.1
1.55	144.7 143.8 143.8	144.1

B

Conc. $AgNO_3$ (millimols per litre)	E.m.f. (millivolts)	Mean
0.19	159.9 159.9 161.7 159.9 159.0 159.0	159.9
0.39	138.3 138.3 140.2 137.2 136.3 138.1	138.1
0.51	127.4 128.2 130.1	128.6

C

Conc. CrO_4 as K_2CrO_4	Conc. CrO_4 as Ag_2CrO_4	Total conc. CrO_4	E.m.f. (m.v.)
1.03	0.20	1.23	136.6
1.37	0.17	1.54	142.1
1.55	0.16	1.71	144.1

Hence when total conc. CrO_4 = 1.55 millimols per litre, e.m.f. = 142.2 millivolts.

TABLE X o.

p_H = 4.3. Conc. gelatin = 0.91 per cent.

A

Conc. K_2CrO_4 (millimols per litre)	E.m.f. (millivolts)	Mean
1.61	124.6 123.7 125.5	124.6
1.89	132.6 131.7 130.8	131.7
2.47	136.2 139.0 138.0	137.7

B

Conc. $AgNO_3$ (millimols per litre)	E.m.f. (millivolts)	Mean
0.46	139.9 138.0 139.0	139.0
0.59	134.4 132.6 134.4	133.8
0.86	121.4 120.6 122.4	121.5

C

Conc. CrO_4 as K_2CrO_4	Conc. CrO_4 as Ag_2CrO_4	Total conc. CrO_4	E.m.f. (m.v.)
1.61	0.40	2.01	124.6
1.89	0.31	2.20	131.7
2.47	0.24	2.71	137.7

Hence when total conc. CrO_4 = 2.14 millimols per litre,

e.m.f. = 130.6 millivolts.

TABLE X p.

p_H = 4.3. Conc. gelatin = 1.49 per cent.

A

Conc. K_2CrO_4 (millimols per litre)	E.m.f. (millivolts)	Mean
2.17	130.2 132.0 130.2	130.8
2.71	134.7 134.7 133.8	134.4

B

Conc. $AgNO_3$ (millimols per litre)	E.m.f. (millivolts)	Mean
0.43	148.5 150.3 148.5	149.1
0.65	135.6 133.8 133.8	134.4
0.93	126.5 126.5 124.7	125.9

C

Conc. CrO_4 as K_2CrO_4	Conc. CrO_4 as Ag_2CrO_4	Total conc. CrO_4	E.m.f. (m.v.)
2.17	0.37	2.54	130.8
2.71	0.33	3.04	134.4

Hence when total conc. CrO_4 = 2.50 millimols per litre,

e.m.f. = 130.5 millivolts.

Potentials in aqueous solutions of potassium chromate saturated with silver chromate. - In order to interpret the e.m.f. values obtained for the equilibrium mixtures, a series of similar experiments on pure aqueous systems was carried out. The general procedure consisted in saturating solutions of potassium chromate with solid silver chromate under the conditions already described. The e.m.f. values obtained are given in Table XI , along with (second column) the final concentrations of chromate in the saturated solutions, estimated as follows.

Three determinations of the e.m.f. for a 0.0004 M. solution of silver nitrate gave the values 133.0, 134.9, and 135.8 millivolts; mean = 134.6 millivolts. On the assumption that the value of the activity coefficient for the silver ion in 0.1 M silver nitrate is 0.77 (Lewis and Randall loc.cit.), the value of a_{Ag^+} corresponding to an e.m.f. of 134.6 millivolts is 0.0004, i.e. numerically identical with the concentration of silver. Now we may consider that for all practical purposes the silver chromate in the solutions in Table XI is completely ionised. It follows then that the chromate concentration (in millimols per litre) in a given case is equal to concentration of potassium chromate + $\frac{1}{2}$ concentration of silver calculated from the appropriate e.m.f. as

just described.

In order to cover the entire range of e.m.f. values obtained with the equilibrium solutions in the case of $p_H = 4.3$, measurements were made on the system obtained by saturating 0.0004 M. silver nitrate with silver chromate. The e.m.f. for this system (124.0 millivolts) gives the total concentration of silver present, viz. 0.614 millimols per litre. Of this, 0.4 millimols per litre is due to silver nitrate (see above). Hence 0.214 millimols per litre is present as silver chromate, and the concentration of chromate is therefore $\frac{0.214}{2} = 0.107$ millimols per litre.

Abegg and Cox [1], in an endeavour to determine the solubility of silver chromate, used an electrode of silver, plated with silver chromate and immersed in 0.05 M K_2CrO_4. They state that the electrode potential was very uncertain, sometimes decreasing suddenly by as much as 20 millivolts, and suggest that the potential involved was not that of Ag (metal)/Ag (ion). In contrast with their experience and in confirmation of that of Bolam and Mackenzie (loc.cit.), the potentials obtained in the present work were steady and reproducible.

The e.m.f. obtained for a saturated solution of silver chromate in distilled water (pH = 6.0 - 6.5)

(1) Abegg and Cox, Zeitschr.f.physik.Chem. 46 (1903) 6.

is in good agreement with that observed by Bolam and Mackenzie (loc.cit.), the values being 148.1 and 147.4 millivolts respectively.

For the purpose of securing a sufficiently definite null point, 0.01 M potassium nitrate was added in the cases where potassium chromate was either absent or present only in very low concentration. Any effect of the potassium nitrate upon the value of a_{Ag^+} was negligible, compared with the experimental error.

TABLE XI

E.m.f. values for aqueous solutions of potassium chromate saturated with silver chromate at 25.0°C.

p_H of system	Conc. of CrO_4 as K_2CrO_4 (millimols per litre)	Final Conc. of CrO_4	E.m.f. (millivolts)	Mean
6.0 - 6.5	1.66	1.69	185.2 185.6 185.6	185.5
	1.00	1.04	178.6 179.6 178.9	179.0
	0.50	0.549	172.4 171.5 171.5	171.8
	0.00	0.120	148.7 148.4 148.9 147.3 147.3 148.2	148.1
5.3	0.00	0.130	146.8 146.8 145.0	146.2
5.0	0.00	0.131	145.0 145.9 146.8	145.9
4.7	1.66	1.69	185.2 186.1 187.1	186.1
	0.50	0.549	171.5 172.4 170.6	171.5

TABLE XI (continued)

p_H of system	Conc. of CrO_4 as K_2CrO_4 (millimols per litre)	Final Conc. of CrO_4	E.m.f. (millivolts)	Mean
4.7	0.20	0.289	156.8 155.0 156.8	156.2
	0.10	0.214	149.5 149.5 149.5	149.5
	0.00	0.153	142.2 140.5 143.2	142.0
4.3	1.66	1.69	185.4 183.5 183.5	184.1
	0.50	0.557	168.1 166.3 168.1	167.5
	0.20	0.302	153.2 151.4 152.3	152.3
	0.10	0.232	144.0 145.8 147.7	145.8
	0.00	0.195	136.8 134.9 135.8	135.8
	0.4 millimols $AgNO_3$	0.107	124.0 124.0 124.0	124.0

Experiments with hydrolysed gelatin. - A three per cent. solution of gelatin (C) was heated on a steam bath for one hour in a small silica flask, fitted with a Pyrex reflux condenser to minimise evaporation. During the heating the solution was frequently shaken. As the result of this treatment the p_H increased from 5.3 to 5.5 - 5.6.

The inhibiting action of this gelatin was determined in the usual way (see page 10), and the following results obtained.

x ($\times 10^2$)	z	y	1	2	3
1.0	3.0	4.8	+	+	+
		5.0	+	-	+
		5.2		-	-
		5.4		-	-

The value of y^x under the particular conditions was therefore taken as being 5.1 c.c., which gives an inhibition value of 1.28 per cent. when the concentration of silver chromate is 1.24 millimols per litre.

E.m.f. measurements were made on the following systems.

(a) 1.22 per cent.gelatin + 2.60 millimols per litre $AgNO_3$.

(b) 1.22 per cent.gelatin + 1.30 millimols per litre K_2CrO_4. saturated with silver chromate at 25.0°C.

Two samples of hydrolysed gelatin were used in each case, and the following results obtained.

(a)		(b)	
millivolts		millivolts	
102.8	101.0	172.6	175.3
101.9	101.0	174.5	175.3
100.9		173.6	174.4
Mean 101.5		174.3	

DISCUSSION

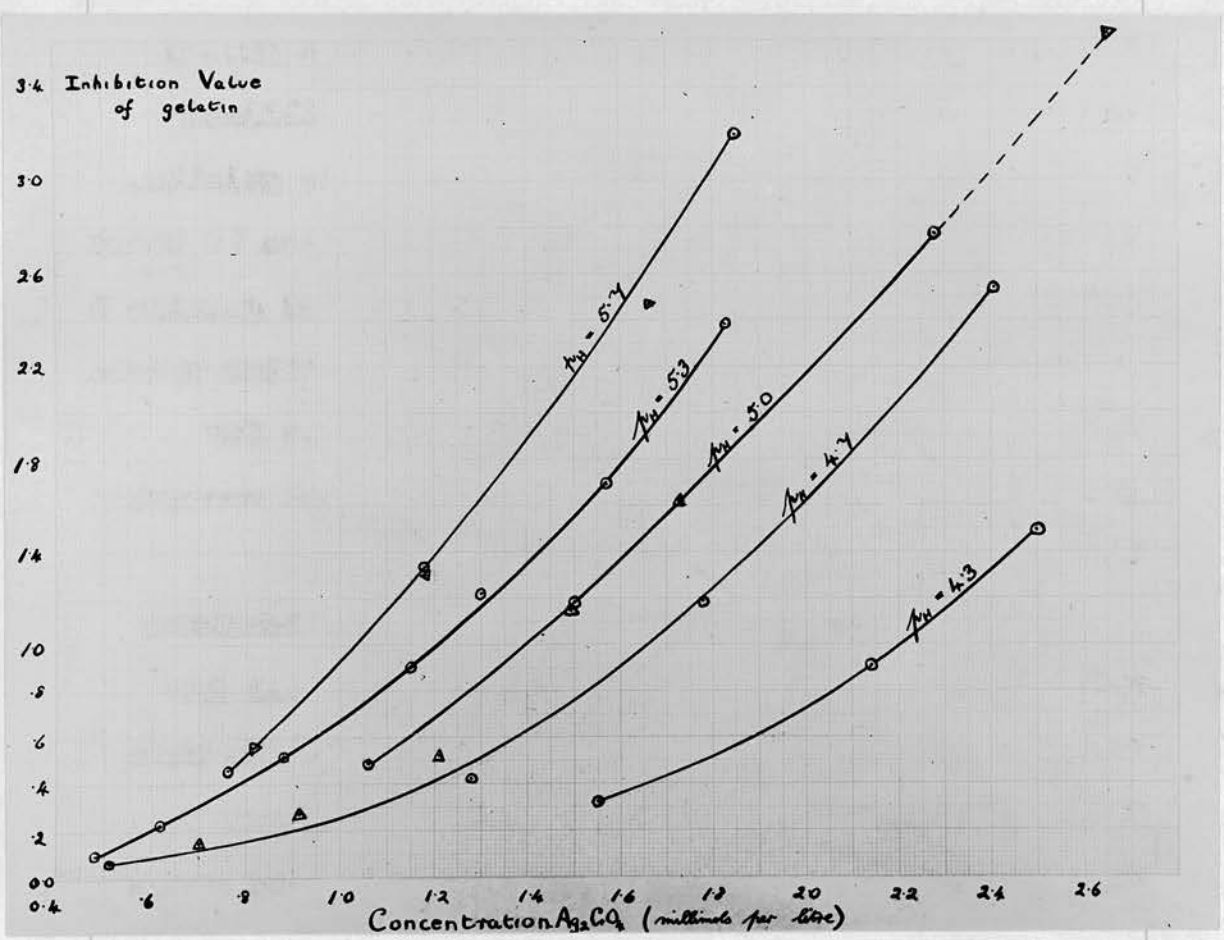

Fig. 4.

△ = Gelatins A and B

⊙ = Gelatin C.

Reproducibility of phenomena

It is of primary importance to enquire how far the data obtained in the present investigation agree with the results of the earlier work. The inhibition values for gelatin A and B are therefore shown in Fig.4, along with the inhibition curves for gelatin C. (Data in Table II). Gelatin A gave a p_H value of 5.0 and it will be seen that Williams and Mackenzie's[1] inhibition values for this gelatin, without addition of acid or alkali, lie close to those for gelatin C at $p_H = 5.0$. Again, untreated gelatin B gave a p_H value of 5.7 - 5.8 and its inhibition values, due to Bolam and Mackenzie,[2] are near those for gelatin C at $p_H = 5.7$, except at the highest concentration, where the agreement is only fair.

Bolam and Mackenzie's (loc.cit.) inhibition values for gelatin A at $p_H = 4.7$, however, all lie somewhat above the 4.7 curve for gelatin C. In this case gelatin A was treated with acetic acid and then washed with water for 3 to 5 days, in order to remove salt impurities, Although the washing was carried out at a relatively low temperature (that of tap water) it is probable that a certain amount of hydrolysis of the gelatin took place and, as will be discussed later, hydrolysis has the effect of raising the inhibition value. It therefore appears likely

(1) Williams and Mackenzie, J.C.S., 117 (1920) 844.
(2) Bolam & Mackenzie. Trans.Farad.Soc., 22 (1926) 151. It should be mentioned that the Graph III for gelatin B shown in Fig.1 of this paper is in error owing to incorrect plotting of the point corresponding to the highest conc. of gelatin investigated.

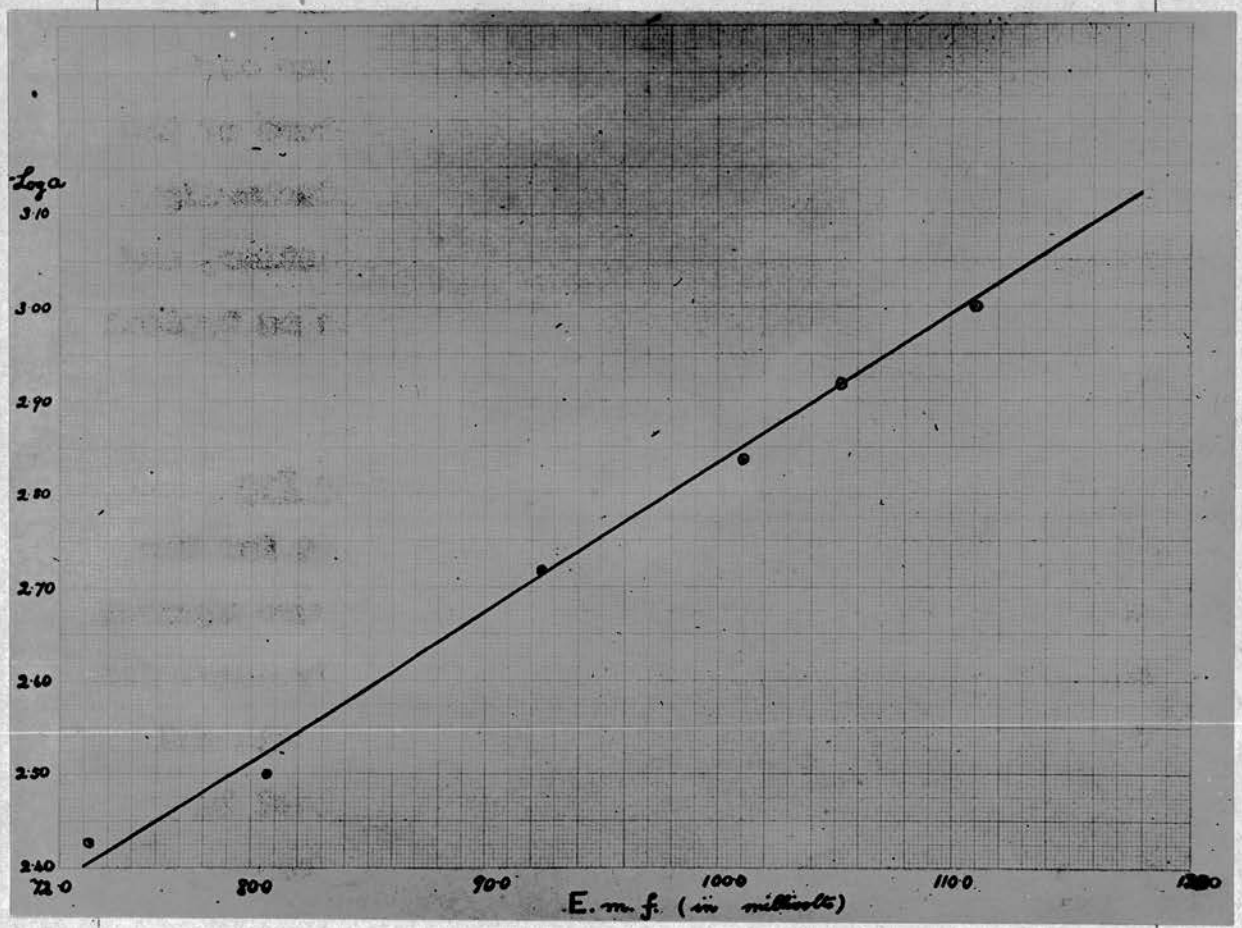
Log a
3·10
3·00
2·90
2·80
2·70
2·60
2·50
2·40
700
800
900
1000
1100
E. m. f. (in millivolts)

Fig. 5.

that if gelatin A had been brought to 4.7 by the simple addition of acetic acid, the agreement with gelatin C would have been close.

From the above we may fairly conclude that at the same temperature and p_H, and under conditions which exclude hydrolysis, gelatins A, B, and C give the same inhibition value to within a few per cent. It follows that, (1) the method of manufacture of the gelatins leads to a product which is satisfactorily reproducible in respect to the inhibitive action, and (2) the behaviour of gelatin C may be taken as typical of that of a high grade material.

Combination between Gelatin and Silver Ion

It will be assumed that the values for the activity coefficient of the silver ion in pure aqueous solutions of silver nitrate are sufficiently near, for the present purpose, to those proposed by Lewis and Randall[1]. On plotting the e.m.f.'s obtained in aqueous solutions (Table III) against the corresponding values of - log a_{Ag^+} calculated on the above assumption (Table IV), the linear curve shown in Fig.5 is obtained.

It would appear from the work of Cumming(2) that 10 M. ammonium nitrate reduces the liquid-liquid junction potential in silver nitrate concentration

(1) Lewis and Randall, "Thermodynamics" (1930).
(2) Cumming, Trans.Farad.Soc., 2 (1906) 213.

cells to a fraction of a millivolt. At 25.0°C. he obtained 0.0556 volt for the cell 0.1M - 0.01 M, and 0.0579 volt for 0.01 M - 0.001M, whereas the values calculated from Lewis and Randall's figures are 0.0551 volt and 0.0572 volt respectively.

There appear to be no adequate grounds for supposing that the gelatin modifies the liquid-liquid potential to any appreciable extent. At the concentrations concerned (up to 3 per cent.), the gelatin has little influence on the diffusibility or electrical mobility of electrolytes. Also a membrane potential [1] of any importance seems unlikely at the high concentration of ammonium nitrate employed. Moreover Sackur[2] has observed that the interposition of a gelatin gel containing lithium chloride and potassium nitrate (at various concentrations) between two aqueous solutions of the same salts gave a net liquid-liquid potential of the same value as that existing in the absence of any intermediate solution, and Salmon[3] that the diffusion potential at the junction NaCl/Sodium oleate was unaffected by gelatin of the soap.

The curve in Fig. 5 may therefore be taken as representing the relation between observed e.m.f. and a_{Ag^+} in mixtures of gelatin and silver nitrate. In Table XII are given the values of a_{Ag^+} for a

(1) Bolam, "The Donnan Equilibria" (Bell 1932) 64.
(2) Sackur, Zeitschr.f.physik.Chem., 38 (1901) 129.
(3) Salmon, J.C.S., 117 (1920) 530.

series of such mixtures, derived from the e.m.f. data in Table VI by interpolation. The last column of Table XII contains the values of a_{Ag^+} for the corresponding pure aqueous solutions of silver nitrate calculated by the aid of Lewis and Randall's coefficients. It will be seen that the activity of the silver ion is depressed by the gelatin, in some cases to a very large extent. Similar results have been recorded by Audubert[1], Northrop and Kunitz,[2] and Kruyt and Boelman[3].

This decrease in activity could be attributed to interionic action, or to combination between the gelatin and the silver ion, or to the operation of both these factors. In all probability gelatin gives rise to polyvalent ions, and it might well be supposed that although the concentration of the protein in the system under consideration is small, the ionic strength is relatively large. Simms[4] however has brought forward cogent argument to the effect that the charged groups in the "dissolved" gelatin molecule are separated by such large distances that the effective valence in acid solution is only 1.8. We may therefore reasonably regard the decrease in a_{Ag^+} on the addition of gelatin as due essentially to actual combination between the gelatin and the silver.

(1) Audubert, Comptes Rendus, 12 (1923) 838.
(2) Northrop and Kunitz, J.gen.Physiol. 9 (1925-26) 351.
(3) Kruyt and Boelman, Koll.Beih. 35 (1932) 165.
(4) Simms, J.gen.Physiol. 11 (1927-28) 613.

TABLE XII.

Activities of silver ion in mixtures of silver nitrate and gelatin (p_H = 5.3)

Conc. $AgNO_3$ (millimols per litre)	Conc. gelatin (per cent.)	E.m.f. (millivolts)	a_{Ag^+} ($\times 10^3$)	
			Gelatin soln.	Aqueous soln.
0.96	0.10	117.3	0.78	0.94
1.75	0.51	110.1	1.01	1.69
2.60	1.22	103.4	1.31	2.48
2.78	1.37	103.9	1.27	2.65
3.13	1.69	104.1	1.26	2.97
3.65	2.38	104.0	1.27	3.44

Activity of Silver Ion in "Critical Mixtures"

As previously defined, a critical mixture is one containing equivalent concentrations of silver nitrate and potassium chromate, together with just sufficient gelatin to prevent any visible change in 72 hours. The question arises, as to whether the value of a_{Ag^+} in such a mixture differs from that in a mixture identical with the critical mixture in regard to gelatin, and silver nitrate content, but containing no potassium chromate. Table XIII shows that the e.m.f. is the same in the two cases. This means either (1) that the presence of potassium chromate is without influence on the value of a_{Ag^+}, and also produces no measurable diffusion potential, or (2) that it alters the value of a_{Ag^+} but at the same time gives rise to a diffusion potential of such dimensions that the net effect on the e.m.f. is negligible. Since the second alternative seems very improbable, these experiments demonstrate that when equivalent concentrations of potassium chromate and silver nitrate are brought together in the presence of gelatin of such concentration that no visible change takes place in 72 hours, the activity of the silver ion has the same value as in the absence of the chromate.

TABLE XIII.

Effect of potassium chromate on the activity of the silver ion in mixtures of silver nitrate and gelatin.

Conc. of $AgNO_3$ (millimols per litre)	E.m.f.* (millivolts) with K_2CrO_4	E.m.f./ (millivolts) without K_2CrO_4
0.96	116.6	117.3
1.75	108.7	110.1
2.60	104.3	103.4
2.78	104.1	103.9
3.13	104.2	104.1
3.65	103.9	104.1

* See Table V

/ See Table VI

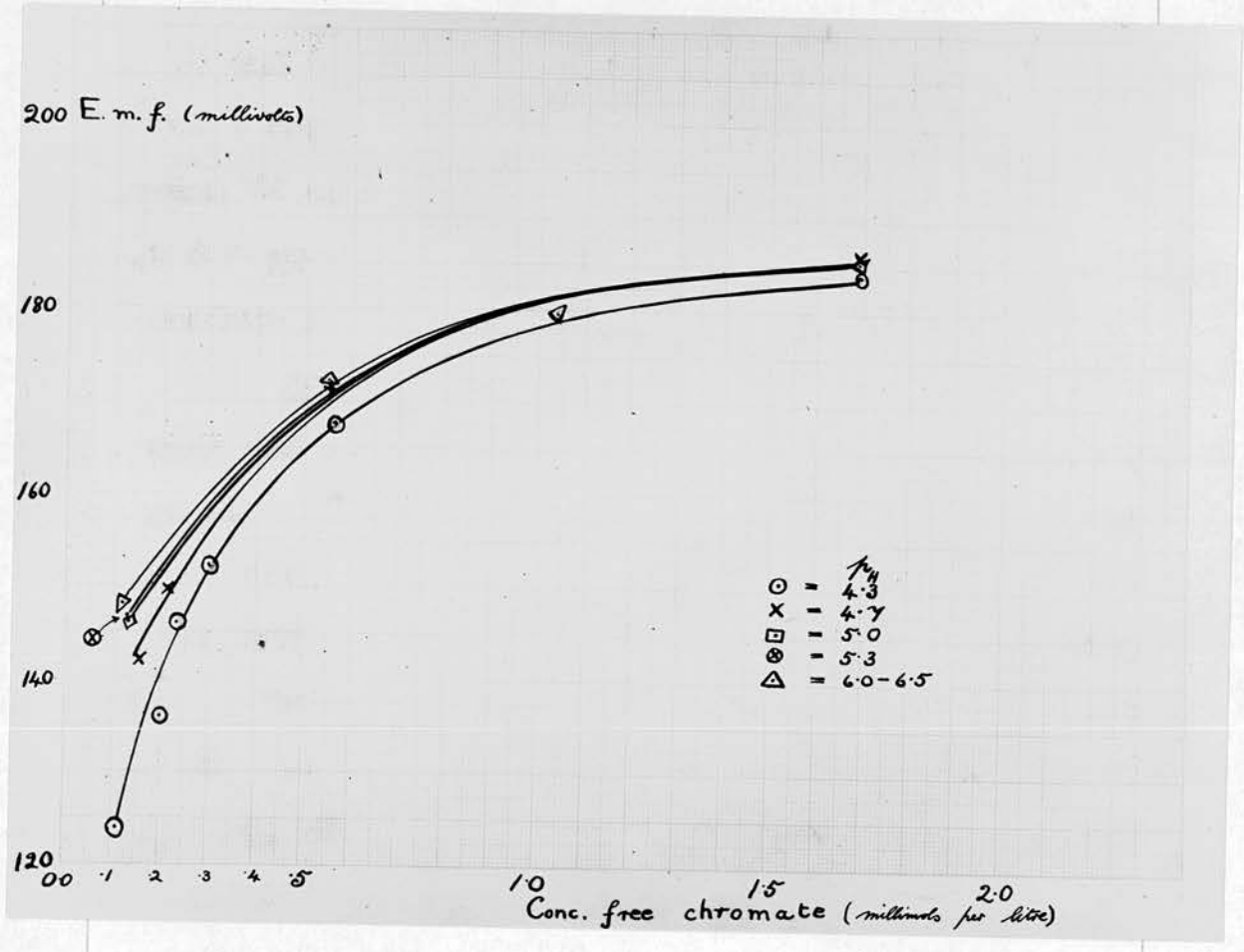
200 E. m. f. (millivolts)
180
160
140
120
00
·1
·2
·3
·4
·5
1·0
1·5
2·0
Conc. free chromate (millimols per litre)
pH
⊙ = 4·3
× = 4·7
⊡ = 5·0
⊗ = 5·3
△ = 6·0 – 6·5

Fig. 6.

Bolam and Mackenzie [1] obtained the values 0.99, 0.99 and 1.01[2] for the activity of the silver ion in three critical systems containing gelatin at $p_H = 5.75$. These agree fairly well with the values for the similar systems containing gelatin at $p_H = 5.7$ (Table XV). On the basis of their results, Bolam and Mackenzie suggested that the value of a_{Ag^+} in critical mixtures becomes constant above a certain concentration of gelatin. As Table XV shows, this holds good at $p_H = 5.3$ and perhaps at $p_H = 5.7$, but is certainly not true for the more acid systems.

Combination of Gelatin with Chromate Ion

It is evident that the e.m.f. in the case of an equilibrium system, i.e. a system produced by saturating a mixture of potassium chromate and gelatin with silver chromate, depends upon the concentration of free chromate ion in the mixture. The graphs in Fig.6, obtained by plotting the data in Table XI give the relation between chromate ion concentration and e.m.f., for systems produced by saturating aqueous solutions of potassium chromate (or silver nitrate) with silver chromate. Since the presence of the gelatin may be considered as exercising no appreciable influence upon conditions at the liquid-liquid junction, these graphs may be employed

(1)Bolam & Mackenzie, Trans.Farad.Soc., 22 (1926) 162.
(2)Recalculated on the assumption that the activity coefficient in 0.1 M $AgNO_3$ is 0.77 and not 0.814 as assumed in the paper.

TABLE XIV.

Concentration of free chromate in critical mixtures

p_H of gelatin	Conc. gelatin (per cent.)	Total conc. of CrO_4 (millimols per litre)	E.m.f. (millivolts)	Conc. of free CrO_4 (millimols per litre)
5.7	0.46	0.76	167.6	0.45
	1.34	1.18	169.4	0.50
5.3	0.10	0.48	166.3	0.43
	0.51	0.88	165.1	0.41
	1.22	1.30	166.3	0.43
	1.69	1.57	165.0	0.41
5.0	0.49	1.06	163.3	0.39
	1.18	1.50	155.6	0.26
4.8 - 4.9	0.47	1.11	161.9	0.36
	1.16	1.58	151.1	0.22
4.7	0.07	0.51	165.3	0.45
	0.42	1.28	152.6	0.25
	1.19	1.78	142.8	0.15
4.3	0.32	1.55	142.2	0.21
	0.91	2.14	130.6	0.14
	1.49	2.50	130.5	0.14

to derive the concentrations of chromate ion in the equilibrium mixtures corresponding to critical mixtures, from the final e.m.f. values given at the bottom of Tables (Xa - Xp). The last column of Table XIV contains the values for concentration of free chromate arrived at in this fashion, and comparison with the figures in the third column of the same Table, reveals that in all cases there is combination between the gelatin and chromate, and that in many instances it is very marked.

Existence of Supersaturation

In Table XV are given the values of a_{Ag^+} for the critical mixtures, derived from the e.m.f. data in Table V by means of the curve in Fig.5. Table XVI gives the values of a_{Ag^+} for the equilibrium mixtures, calculated from the appropriate e.m.f. data (Tables X & XIV) on the assumption that the activity coefficient of the silver ion is unity at the very low concentrations concerned (see page 60) and taking the activity coefficient in 0.1M silver nitrate as 0.77.

Comparison of the two sets of values (Table XVII) reveals that the activity of the silver ion in a given critical system is always very much (six to ten fold) greater than in the corresponding equilibrium

TABLE XV.

Activity of silver ion in critical mixtures

p_H	Conc. of gelatin (per cent.)	E.m.f. (millivolts)	a_{Ag^+} ($\times 10^3$)
5.7	0.46	111.6	0.96
	1.34	108.2	1.09
	3.20	109.9	1.02
5.3	0.10	116.6	0.79
	0.22	113.2	0.90
	0.51	108.7	1.06
	0.90	104.7	1.24
	1.22	104.3	1.25
	1.37	104.1	1.26
	1.48	103.9	1.27
	1.69	104.2	1.26
	1.97	103.9	1.27
	2.38	103.9	1.27
5.0	0.49	99.9	1.47
	1.18	96.1	1.69
	2.77	93.4	1.87
4.8 - 4.9	0.47	99.7	1.49
	1.16	94.1	1.82
4.7	0.07	112.9	0.91
	0.42	96.6	1.66
	1.19	92.3	1.95
	2.54	86.2	2.44
4.3	0.32	88.1	2.27
	0.91	81.1	2.95
	1.49	75.0	3.68

TABLE XVI

Activity of silver ion in "equilibrium systems"

p_H of gelatin	Conc. of gelatin (per cent.)	E.m.f. (millivolts)	a_{Ag^+} ($\times 10^3$)
5.7	0.46	167.6	0.112
	1.34	169.4	0.105
5.3	0.10	166.3	0.118
	0.51	165.1	0.124
	1.22	166.3	0.118
	1.69	165.0	0.124
5.0	0.49	163.3	0.133
	1.18	155.6	0.180
4.8 - 4.9	0.47	161.9	0.141
	1.16	151.1	0.214
4.7	0.07	165.3	0.123
	0.42	152.6	0.202
	1.19	142.8	0.295
4.3	0.32	142.2	0.302
	0.91	130.6	0.475
	1.49	130.5	0.477

TABLE XVII.

The comparison of the activity of the silver ion in critical mixtures with the activity in equilibrium systems.

p_H	Conc. of gelatin (per cent.)	a_{Ag^+} ($\times 10^3$)		Ratio
		Critical mixtures	Equilibrium systems	
5.7	0.46	0.96	0.112	8.6
	1.34	1.09	0.105	10.4
5.3	0.10	0.79	0.118	6.7
	0.51	1.06	0.124	8.6
	1.22	1.25	0.118	10.6
	1.69	1.26	0.124	10.2
5.0	0.49	1.47	0.133	11.1
	1.18	1.69	0.180	9.4
4.8 - 4.9	0.47	1.49	0.141	10.6
	1.16	1.82	0.214	8.5
4.7	0.07	0.91	0.123	7.4
	0.42	1.66	0.202	8.2
	1.19	1.95	0.295	
4.3	0.32	2.27	0.302	7.5
	0.91	2.95	0.475	6.2
	1.49	3.68	0.477	7.7

system. This proves directly and conclusively that the critical systems are strongly supersaturated with respect to silver chromate.

Condition of Silver Chromate in "Critical Mixtures".

On general grounds it is arguable that the whole of the silver chromate in the critical system is not accounted for by combination of a proportion of the silver and chromate with the gelatin, and the formation of a supersaturated solution by the remainder, but that separation of solid silver chromate to form a highly disperse yellow sol does occur to some extent. The presence of colloidal silver chromate would not necessarily exclude supersaturation. Since the solubility of small particles increases with decrease in size (1) one can conceive of the existence of a sol of such a high degree of dispersion, that the solubility of the silver chromate is raised much above the normal value. Presumably some such state of affairs is pictured by Hedges (2) when he remarks "It is perhaps unwise to attempt to distinguish sharply between the condition of a little-understood, highly supersaturated, "molecular" solution and a highly disperse, colloidal solution". In any

(1) Kolthoff. Journ.Phys.Chem., 36 (1932) 860.
Partington. Ibid. 1853.
Dundon and Mack, J.A.C.S., 45 (1923) 2479.
Dundon. Ibid. 2658.
Partington and Jones, J.C.S. 107 (1915) 1019.
(2) Hedges "Colloids" (Arnold: 1931) 237.

case the adsorption of the gelatin on the sol particles would check their growth and tend to promote supersaturation.

The work of Bolam and Mackenzie [1] and the results of the present investigation show, however, that no measurable amount of solid silver chromate is present. Bolam and Mackenzie found that the activity of the silver ion in a critical system remained quite constant for at least 72 hours. One the other hand, if the concentration of gelatin was reduced, all other factors remaining unchanged, so that visible formation of solid silver chromate occurred, the activity decreased. Moreover the change in a_{Ag^+} undoubtedly ran parallel with the course of precipitation. As the gelatin/silver chromate ratio increased, the rate of decrease in a_{Ag^+} diminished, which can only mean that when the critical ratio is reached, precipitation is at least too slow to be detected, i.e., for all practical purposes does not occur at all. We may therefore say that solid silver chromate is formed only when the system changes in colour from yellow to red. Otherwise the silver salt exists partly in combination with the gelatin and partly in highly supersaturated true solution, i.e., as free simple ions.

(1) Bolam & Mackenzie, Trans.Farad.Soc., 22 (1926) 162.

The fact that the value of a_{Ag^+} in a critical mixture is identical with that in a mixture of the same composition as regards gelatin and silver nitrate, but containing no potassium chromate (see page 76), is obviously in line with the view that no perceptible separation of solid occurs.

In the case of the critical systems examined by Bolam and Mackenzie (loc.cit.), about one third of the total silver was found to be present in the form of free ions.(1) Apropos of this result Chatterji and Dhar(2) remark, "We are of the opinion that the two thirds of the silver, which does not exist in the ionic condition, remain in the colloidal state. Hence the measurements of Bolam and Mackenzie are in support of our views that the sparingly soluble substances formed in the presence of gelatin exist as a colloid." It will be seen that Chatterji and Dhar ignore altogether the possibility of combination of silver and chromate ions with the gelatin, and, in view of the foregoing discussion, it is clear that their interpretation of Bolam and Mackenzie's results is not in agreement with the facts.

Chatterji and Dhar (loc.cit.) also say, "Moreover it should be emphasised that the hydrogen ions present in gelatin exert a solvent action on the

(1) Confirmed in the course of this investigation (see page 78).
(2) Chatterji and Dhar. Journ.Indian Chem.Soc., 5 (1928) 181.

silver chromate formed, because silver chromate dissolves in acids and hence more free silver ions are detected in solution due to the existence of hydrogen ions in the gelatin". The comparison between the values of a_{Ag^+} in critical and equilibrium systems (Table XVII) shows quite definitely that the high concentration of silver ions in the critical mixtures, as compared with that in a pure aqueous solution of silver chromate is not simply the result of increased solubility due to the presence of acid in the gelatin but that it arises mainly from super-saturation.

Inhibitive Action of Gelatin

According to the well-known theory of von Weimann, (1) the initial velocity of condensation of the ions or molecules to form crystallisation centres may be formulated thus :-

$$W = K \frac{\text{Condensation pressure}}{\text{Condensation resistance}} = K \frac{Q - L}{L} = K \frac{P}{L} = Ku$$

where W is the initial velocity of condensation, K is a constant, Q the total concentration of the substance which is to precipitate, L the solubility of coarse crystals of the substance, and $Q - L = P$ the amount of supersaturation. The ratio $P/L = u$ is the degree of supersaturation at the instant condensation begins

(1) Kolloid-Z. 2, 199, 230, 275, 301, 326;
Supplement 2, LII; 3, 89, 282 (1908); 4 27 (1909)
"Grundzüge der Dispersoidchemie" (1911);
"Zum Lehre von dem Züstanden der Materie" (1914).

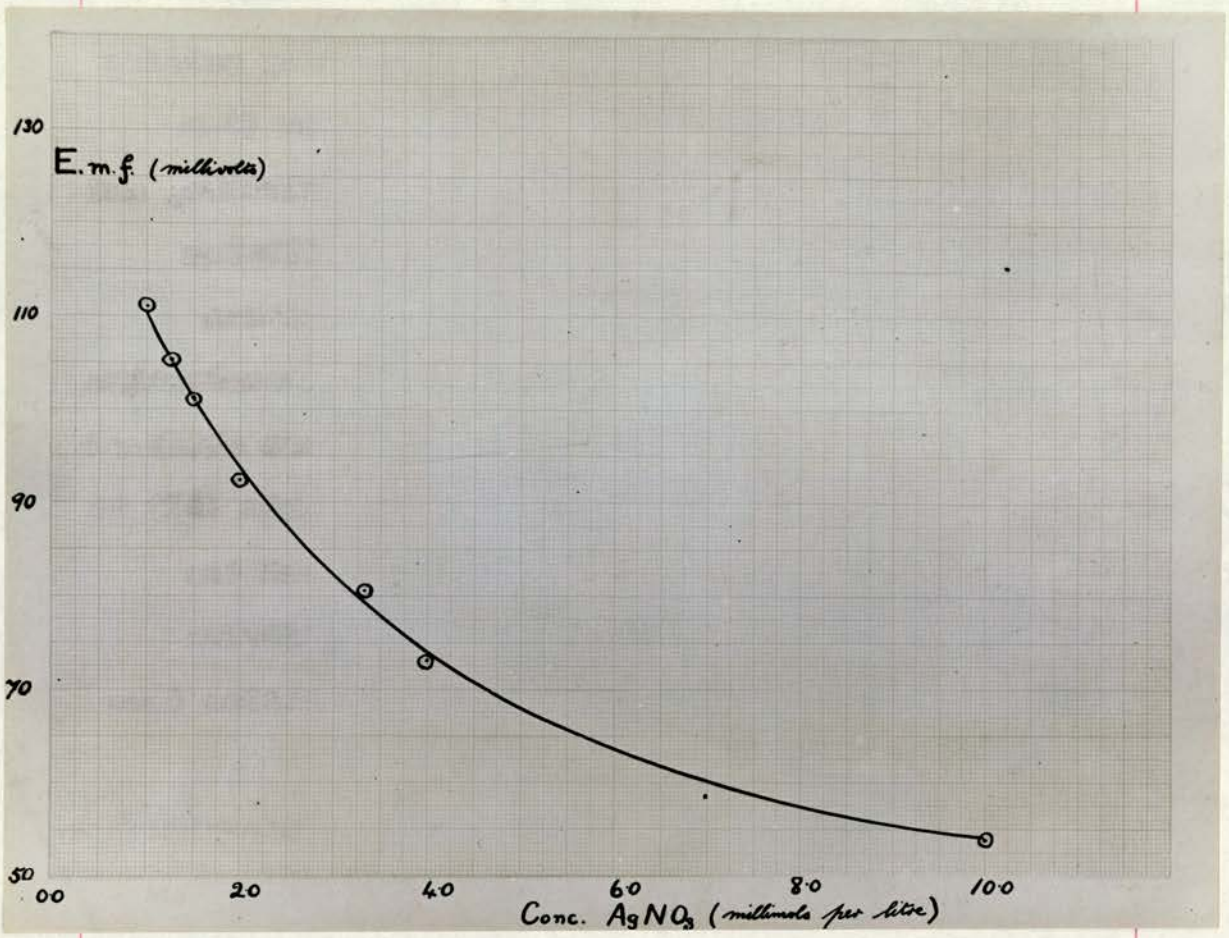
130
E. m. f. (millivolts)
110
90
70
50
00
20
4·0
6·0
8·0
10·0
Conc. AgNO3 (millimols per litre)

Fig. 7.

and may be regarded as a measure of the tendency of the substance to separate in the solid form.

In the present instance, where precipitation does not take place, it is reasonable to suppose that the inhibitive power [1] of the gelatin is proportional to the tendency to precipitate in the absence of gelatin. Moreover it appears feasible to employ a formulation similar to the above by putting Q equal to the concentration of free silver (i.e. uncombined with gelatin) in the critical mixture, and L equal to that in the corresponding equilibrium mixture. Values of Q, L, and u for the systems examined are shown in Table XVIII. The concentration of free silver in the critical mixtures were obtained by applying the graph in Fig.7 (data in Table III) to the appropriate e.m.f. data (Table XV), and the concentrations of free silver in the equilibrium solutions were taken as equal to the activities (see p. 60).

It will be seen that within the experimental error, the value of u is constant at a given p_H for systems whose gelatin content lies between 0.32 and 1.69 per cent. Over this range therefore, the inhibition curve (Fig. 4) represents the compositions of systems with the same degree of supersaturation.

(1) I.e. that power of the gelatin to maintain silver chromate in supersaturated solution. (Term used here in its strict sense.

TABLE XVIII.

Values for degrees of supersaturation in critical mixtures of silver chromate and gelatin.

p_H	Conc. of gelatin (per cent.)	Q	L	u (Degree of supersaturation)	Mean §
5.7	0.46	(0.95)*	0.112	7.5	8.5
	1.34	1.10	0.105	9.5	
5.3	0.10	(0.70)	0.118	4.9	
	0.51	1.10	0.124	7.9	9.1
	1.22	1.30	0.118	10.0	
	1.69	1.30	0.124	9.5	
5.0	0.49	1.55	0.133	10.7	9.9
	1.18	1.80	0.180	9.0	
4.8 - 4.9	0.47	1.55	0.141	10.0	9.1
	1.16	1.95	0.214	8.1	
4.7	0.07	(0.85)	0.123	5.9	
	0.42	1.80	0.202	7.9	7.0
	1.19	2.10	0.295	6.1	
4.3	0.32	2.45	0.302	7.1	6.3
	0.91	3.10	0.475	5.5	
	1.49	3.85	0.477	7.1	

* Values in brackets obtained by extrapolating graph in Fig. 7.

§ **Mean** of values for concentrations of gelatin of 0.32 per cent. and over.

At some lower concentration the degree of supersaturation must decrease, since in the absence of gelatin it is of course nil. On the other hand there is no reason to suppose that it ceases to be constant at higher concentrations of gelatin. It would appear then that the gelatin does not possess unlimited powers of inhibition, but that after a certain concentraion is reached, further addition of gelatin is ineffective. This is consonant with the view that the gelatin acts by virtue of its tendency to be adsorbed by the incipient crystallisation centres, since there must be a limit to the amount of such adsorption. Judging from the "protective" action of gelatin, it is probable that the limit is reached at a comparatively low concentration of that substance.

The mean value of u given in the last column of Table XVIII is in each case the mean of the values for the range of gelatin concentration 0.32 to 1.69 per cent. Judging from these figures it would appear that the inhibitive action increases slightly as the p_H decreases from 5.7 to 5.0 and falls off more rapidly as the p_H is further decreased. It was observed that at $p_H = 5.0$ the gelatin solutions were very turbid compared with solutions at the other p_H values. Kraemer (1) has also observed a very

(1) Kraemer, "Colloid Symposium Monograph" IV (1926) 102.

pronounced maximum in the Tyndall effect at p_H = 5.0, and suggests that this is the true isoelectric point of gelatin. At the present stage, however, it is not possible to do more than point out that there may be some connection between the inhibitive action and the "scattering" phenomena.

Findlay and King[1] found that a gelatin solution which had been heated and then suddenly cooled, affected the evolution of carbon dioxide from supersaturated solution to a more marked degree than a gelatin solution which was slowly cooled. This suggested that the sol form of the gelatin was responsible for the action on the gas. In the present work the gelatin solutions were invariably prepared and used in the same manner. The gelatin was dispersed by heating at 35°C. with constant shaking, so that solution was complete in about fifteen minutes. The warm gelatin was immediately added to the salt solution (at room temperature) and the resulting mixtures kept at 25.0°C. for a few minutes before the final mixing. It would seem that these conditions should if anything favour the gel form of the gelatin, as certainly must the waiting period of 72 hours at 25.0°C. In any case the conditions were uniform throughout the work.

(1) Findlay and King, J.C.S., 105,(1914) 1297.

Effect of Hydrolysis of Gelatin

Bolam and Desai[1] and Nabar and Desai[2] have shown that precipitation of silver chromate occurs more readily in the presence of gelatin which has been hydrolysed, than in the presence of the unhydrolysed material, i.e. the induction period is shorter. The results of the experiments described on page 65 are in line with this. Whereas the "inhibitive value" of unhydrolysed gelatin C is 1.22 when the concentration of Ag_2CrO_4 is 1.30 millimols per litre (Table II), that of the hydrolysed material is 1.28 at a chromate concentration of 1.24 millimols per litre. Thus after hydrolysis more gelatin is required to prevent precipitation at a smaller concentration of insoluble salt.

One obvious explanation of the difference in behaviour produced by the hydrolysis is that the combination between gelatin and silver or chromate is decreased, so that there are more free ions present. That the amount of free silver ion remains unaltered is shown by the fact that the e.m.f. for the system 1.22 per cent. gelatin + 2.60 millimols per litre $AgNO_3$ is 101.5 m.v. (experiment (a) page 65) for hydrolysed gelatin and 104.3 m.v. (Table V, page 27) for unhydrolysed.[3] On the other hand the system -

(1) Bolam and Desai, Trans.Farad.Soc., 24 (1928) 50.
(2) Nabar and Desai, Ibid. 28 (1932) 449.
(3) This agrees with the results of Nabar and Dedai (loc.cit.).

1.22 per cent. hydrolysed gelatin + 1.30 millimols per litre K_2CrO_4 + Ag_2CrO_4 (saturated) gives an e.m.f. value of 174.3 m.v. (experiment (b), page 65), as compared with 167.3 m.v. (Table Xe page 48) for the similar system with the unhydrolysed gelatin. This indicates that there is less combination between chromate and gelatin when the latter is hydrolysed.

It will be noticed that the p_H of the gelatin increased from 5.3 to 5.5 - 5.6 in the course of the hydrolysis. As is shown by the data in Table XIV, increase in p_H is accompanied by increase in free chromate in the case of the unhydrolysed gelatin, and it is possible that hydrolysis does not affect the correlation between these factors. It should be mentioned however, that Bolam and Desai (loc.cit.) observed that restoration of the p_H of the hydrolysed gelatin to its original value (by the addition of acetic acid) did not produce a corresponding change in the behaviour of the gelatin in regard to precipitation.

The available evidence does not enable a decision to be made as to whether the <u>true</u> inhibitive power of the gelatin is affected by the hydrolysis.

SUMMARY

1. The concentrations of a high grade gelatin required to just prevent precipitation at 25.0°C. in 72 hours by the interaction of silver nitrate and potassium chromate in equivalent concentrations, have been determined for various concentrations of silver chromate and at several pH values.

2. Electromotive force measurements with the silver electrode have been made on the following types of system, (1) aqueous solutions of silver nitrate, (2) mixtures of equivalent concentrations of silver nitrate and potassium chromate, containing sufficient gelatin to prevent precipitation, (3) mixtures of gelatin and silver nitrate, (4) mixtures of gelatin and potassium chromate saturated with silver chromate, (5) aqueous solutions of potassium chromate saturated with silver chromate.

3. It is shown that in mixtures of silver nitrate and potassium chromate, containing sufficient gelatin to just prevent visible change in 72 hours, (1) part of the silver and chromate are combined with the gelatin, (2) the remainder exists as free ions, which form a highly supersaturated solution of silver chromate, (3) there is no separation of solid silver

chromate.

4. It is shown that for a given p_H the degree of supersaturation, and therefore the true inhibitive action of the gelatin, becomes constant at some low concentration of gelatin.

5. It is shown that the degree of supersaturation increases as the p_H decreases from 5.7 to 5.0 and then decreases with further decrease in the p_H.

6. It is shown that hydrolysis of the gelatin does not affect the extent of combination with silver but decreases that with chromate. This at least partly accounts for the increase in the concentration of gelatin required to prevent precipitation.

In conclusion, I wish to express my thanks to Dr.T.R.Bolam for his encouragement and valuable guidance, during the course of this work.